Alkanes

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

Hydrocarbons

- **Aliphatic** (*áleiphar* = Ointment (unguento)).
  - 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**

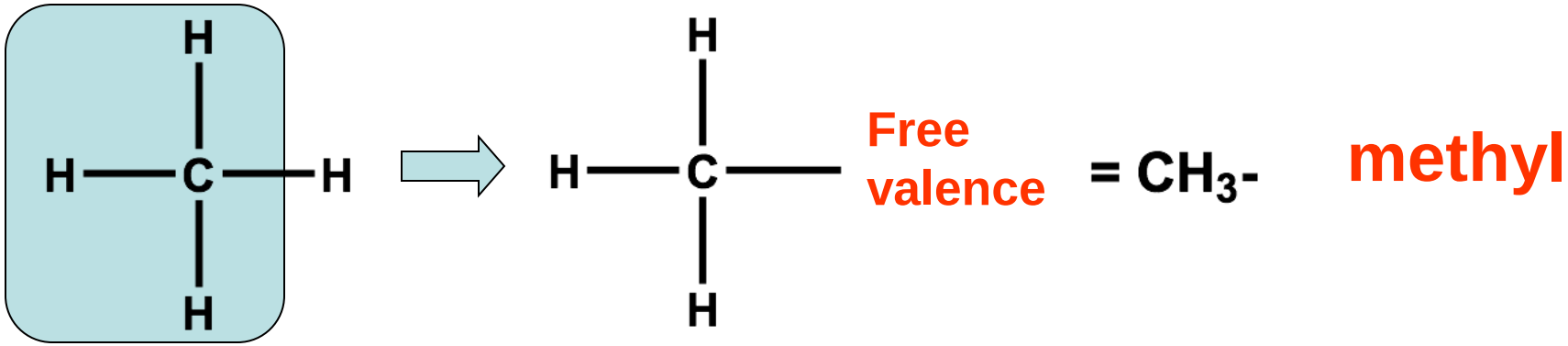
Alkanes

Number of C-atoms	Molecular formula	Name (*n*-alkane)
1	CH_4	methane
2	C_2H_6	ethane
3	C_3H_8	propane
4	C_4H_{10}	butane
5	C_5H_{12}	pentane
6	C_6H_{14}	hexane
7	C_7H_{16}	heptane
8	C_8H_{18}	octane
9	C_9H_{20}	nonane
10	$C_{10}H_{22}$	decane
20	$C_{20}H_{42}$	eicosane

Empirical formula: C_nH_{2n+2}

Alkyl Groups

Root-Suffix (= yl)



$CH_3\text{-}CH_2\text{-}$ = $C_2H_5\text{-}$ **ethyl**

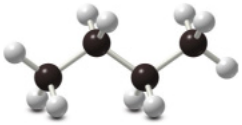
$CH_3\text{-}CH_2\text{-}CH_2\text{-}$ = $C_3H_7\text{-}$ **propyl**

Alkanes – Structural Isomerism

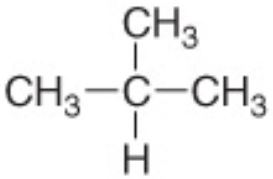
- There are two hydrocarbons with empirical formula C_4H_{10}: butane and isobutane.
- Butane and isobutane are structural isomers: they have the same composition but different physico-chemical properties.

$CH_3CH_2CH_2CH_3$

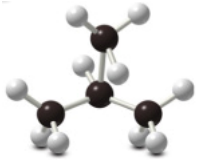
butane



Linear Alkane

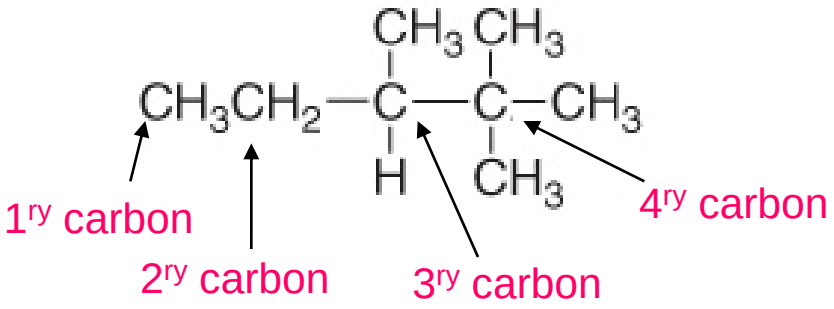


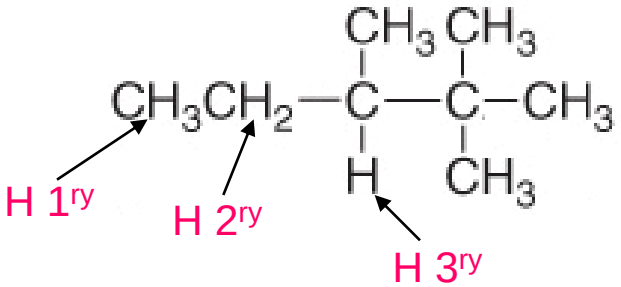
isobutane

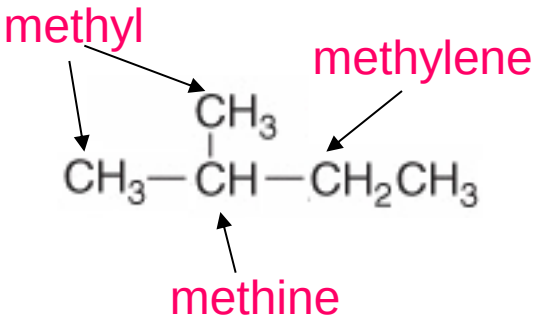


Branched Alkane

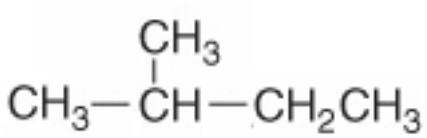
Examples


1ry carbon
2ry carbon
3ry carbon
4ry carbon

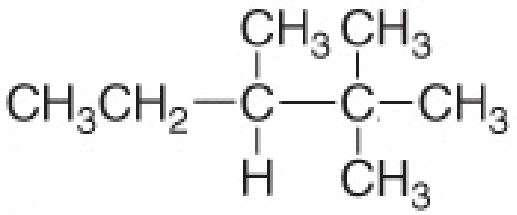

H 1ry
H 2ry
H 3ry


methyl
methylene
methine

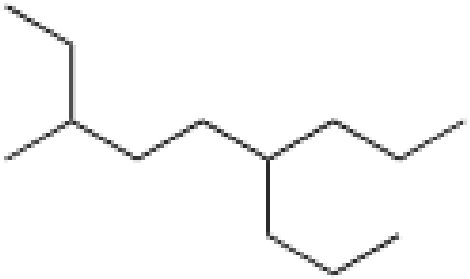
Nomenclature



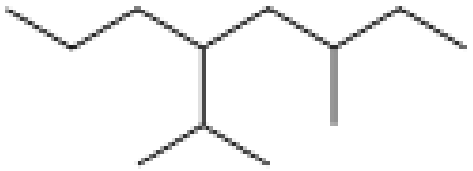
2-metylbutane



2,2,3-trimethylpentane



3-methyl-6-propylnonane



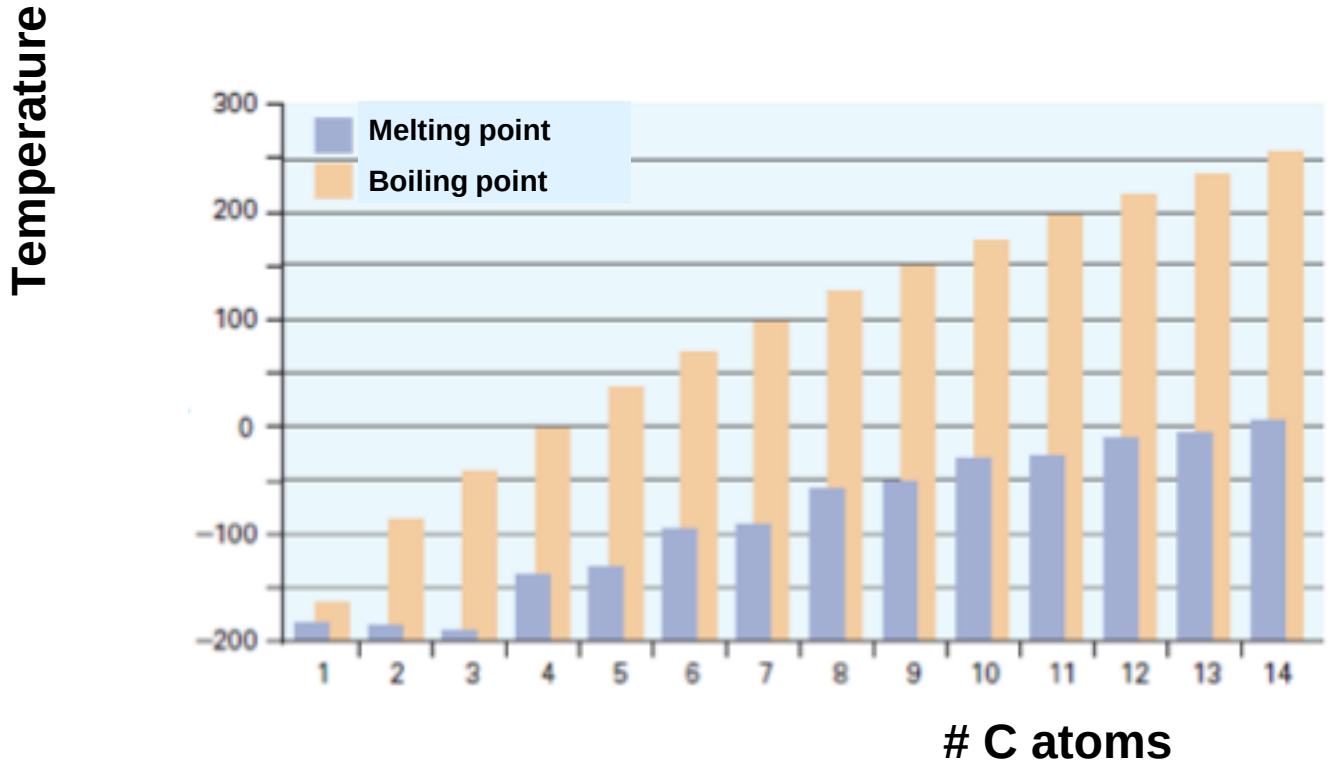
5-(1-methylethyl)-3-methyloctane

Alkyl Groups

C-Atoms	Structure	Name
1	CH_3-	methyl
	$-CH_2-$	methylene
	$-\underset{\displaystyle -}{CH}-$	methine
2	CH_3CH_2-	ethyl
3	$CH_3CH_2CH_2-$	*n*-propyl
	$CH_3\underset{\displaystyle |}{C}HCH_3$	isopropyl
4	$CH_3CH_2CH_2CH_2-$	*n*-butyl
	$CH_3\underset{\displaystyle |}{C}HCH_2-$ $\quad\quad\quad\quad CH_3$	isobutyl
	$CH_3CH_2\underset{\displaystyle |}{C}H-$ $\quad\quad\quad\quad CH_3$	*sec*-butyl
	$CH_3\underset{\displaystyle |}{\overset{\displaystyle CH_3}{C}}-$ $\quad\quad CH_3$	*tert*-butyl

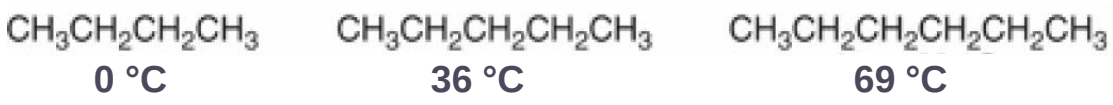
C-Atoms	Structure	Name
5	$CH_3CH_2CH_2CH_2CH_2-$	*n*-pentyl
	$CH_3\underset{\displaystyle |}{C}HCH_2CH_2-$ $\quad\quad\quad CH_3$	isopentyl
	$CH_3\underset{\displaystyle |}{\overset{\displaystyle CH_3}{C}}CH_2-$ $\quad\quad\quad CH_3$	neopentyl
	$CH_3\overset{2}{\underset{\displaystyle |}{C}}HCH_2CH_2CH_3$	
	$CH_3CH_2\overset{3}{\underset{\displaystyle |}{C}}HCH_2CH_3$	*sec*-pentyl

Physical Properties



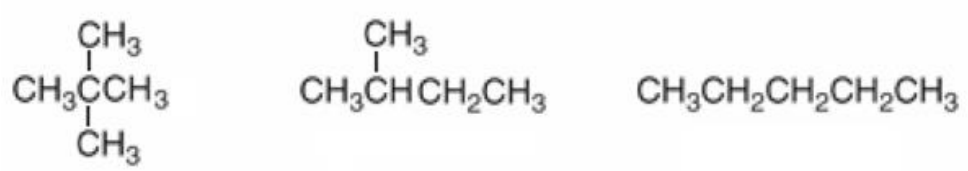
Physical Properties

b.p.



0 °C 36 °C 69 °C

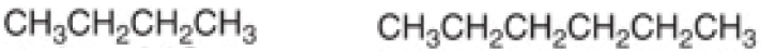
Surface area increases with C-atoms



10 °C 30 °C 36 °C

Surface area decreases with branching

m.p.



–138 °C –95 °C

Surface area increases with C-atoms

–160°C –17 °C

Increases with symmetry

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

Natural Sources

Natural sources of alkanes are natural gas and oil.

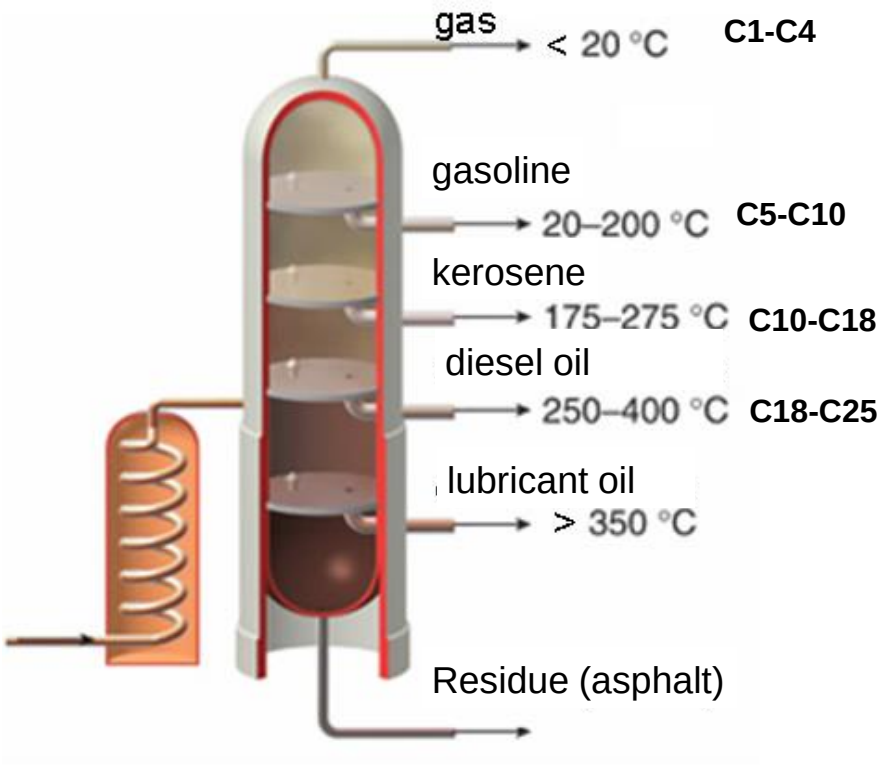
Natural gas contains mainly methane: minor components are ethane, propane and butane.

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.

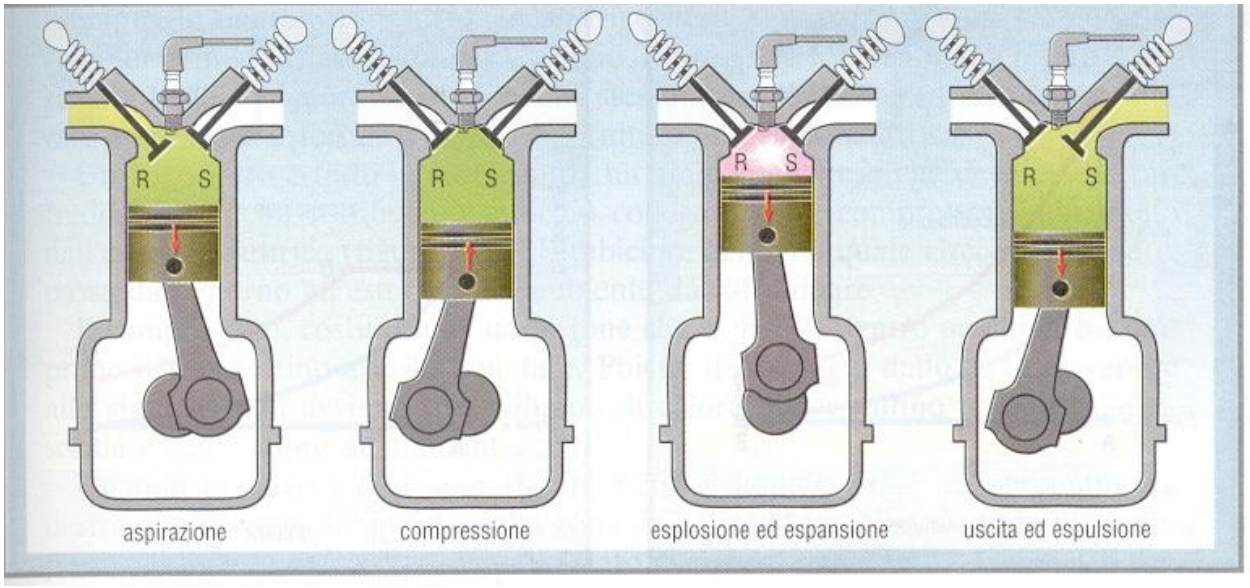
Pre-heated crude oil and gases



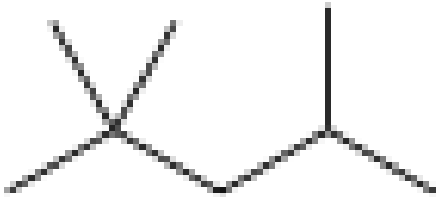
Industrial Treatments of Refined Oil

- 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).

Gasoline – Octane

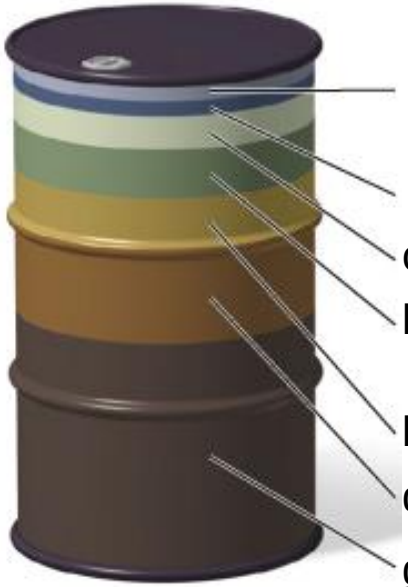


heptane: 0



Isooctane: 100

Crude Oil



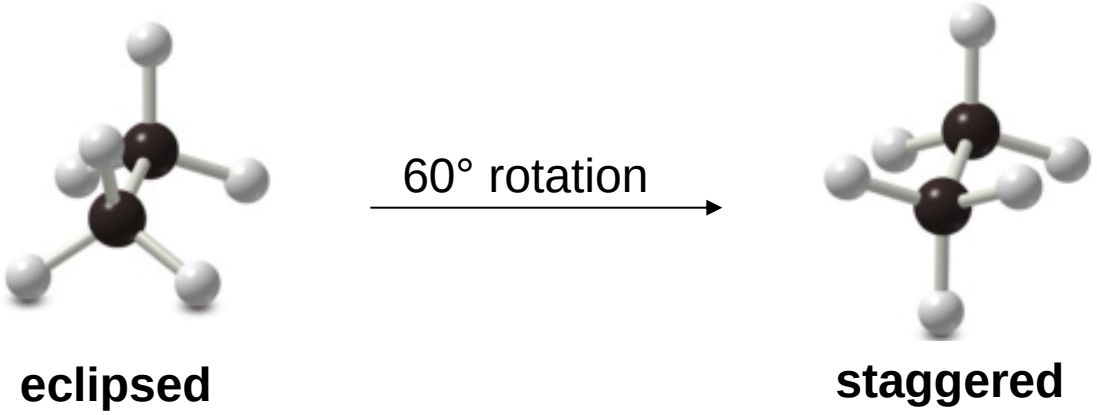
fine chemicals and plastics	1.25 gal	3%
asphalt	1,3 gal	3%
coolants	2,9 gal	7%
lubrificants, waxes, solvents	4,2 gal	10%
kerosene (aeroplanes)	4,2 gal	10%
diesel and fuel oil	8,4 gal	20%
gasoline	19,7 gal	47%

Barrel
42 gal
159 l

1 US gal = 3.78 l

Conformational Isomerism

Ethane



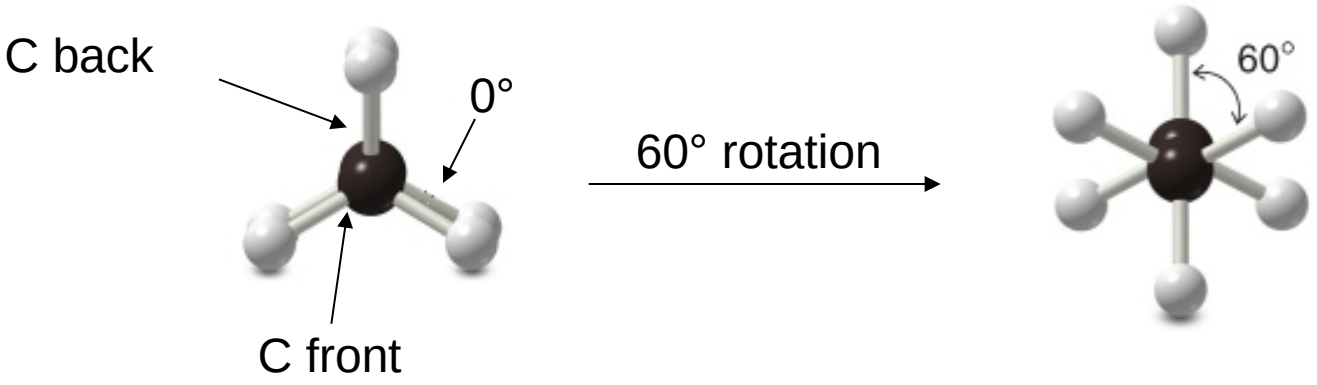
eclipsed **staggered**

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

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



Eclipsed conformation

Staggered conformation

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

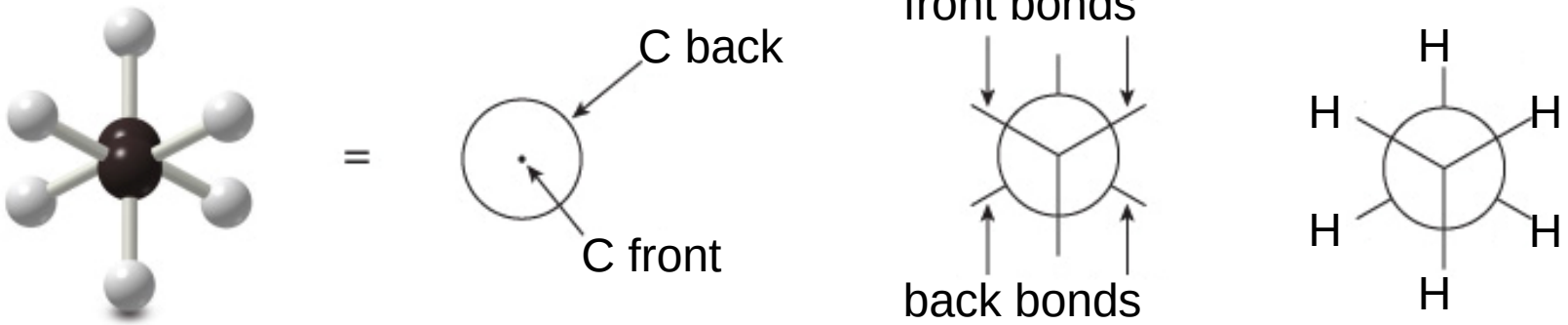
Newman Projection

- 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).

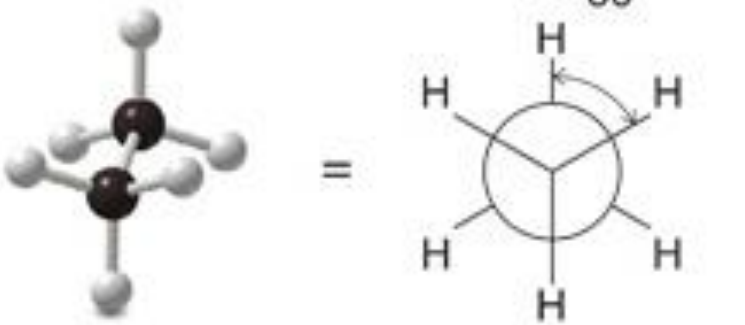
[2] Draw the bonds

[3] Add the atoms

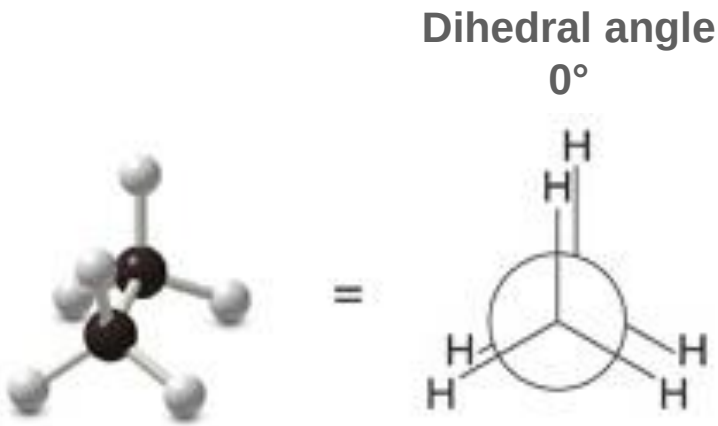


Newman Projections of Ethane

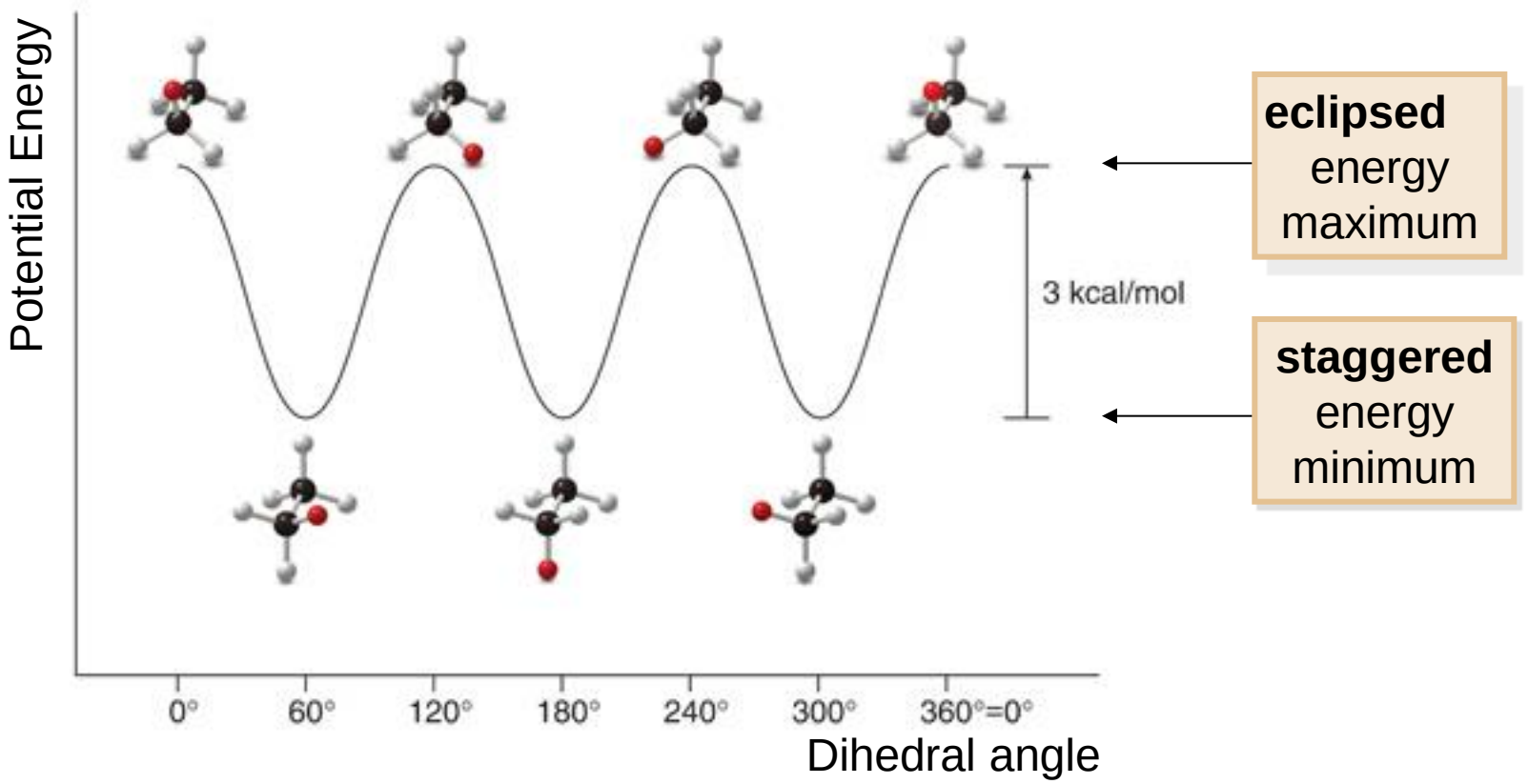
staggered conformation



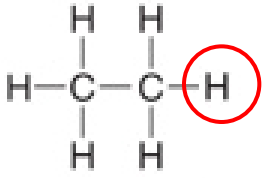
eclipsed conformation



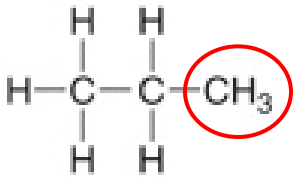
Conformations of Ethane



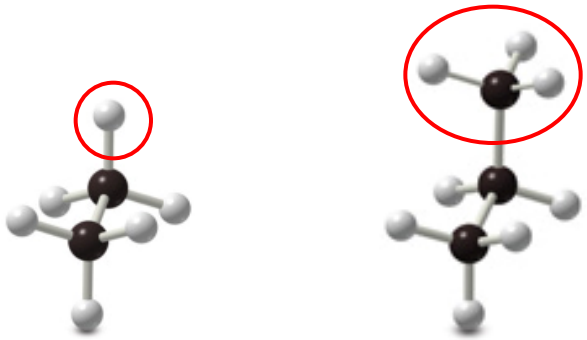
Conformations of Propane

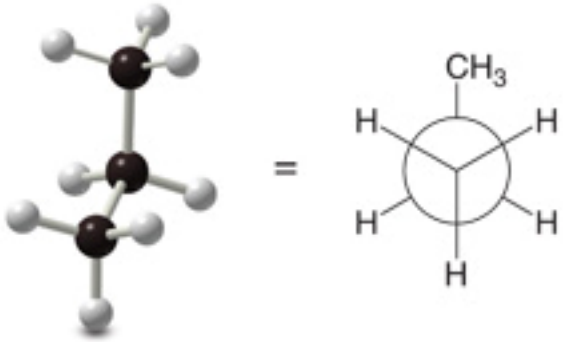


ehtane

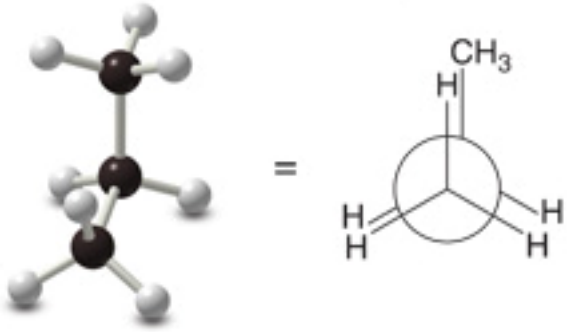


propane



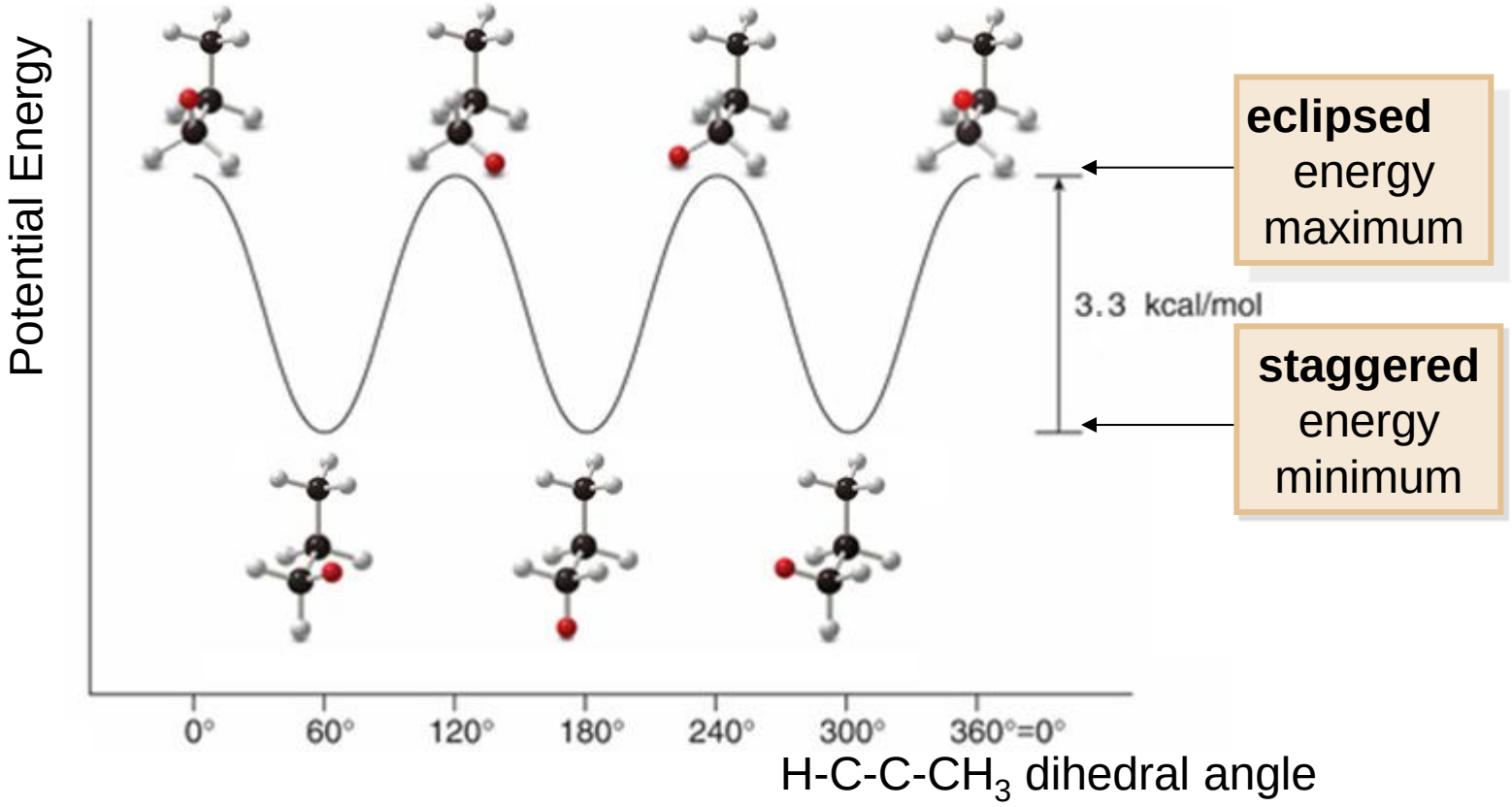


staggered conformation



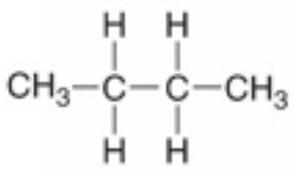
eclipsed conformation

Conformations of Propane

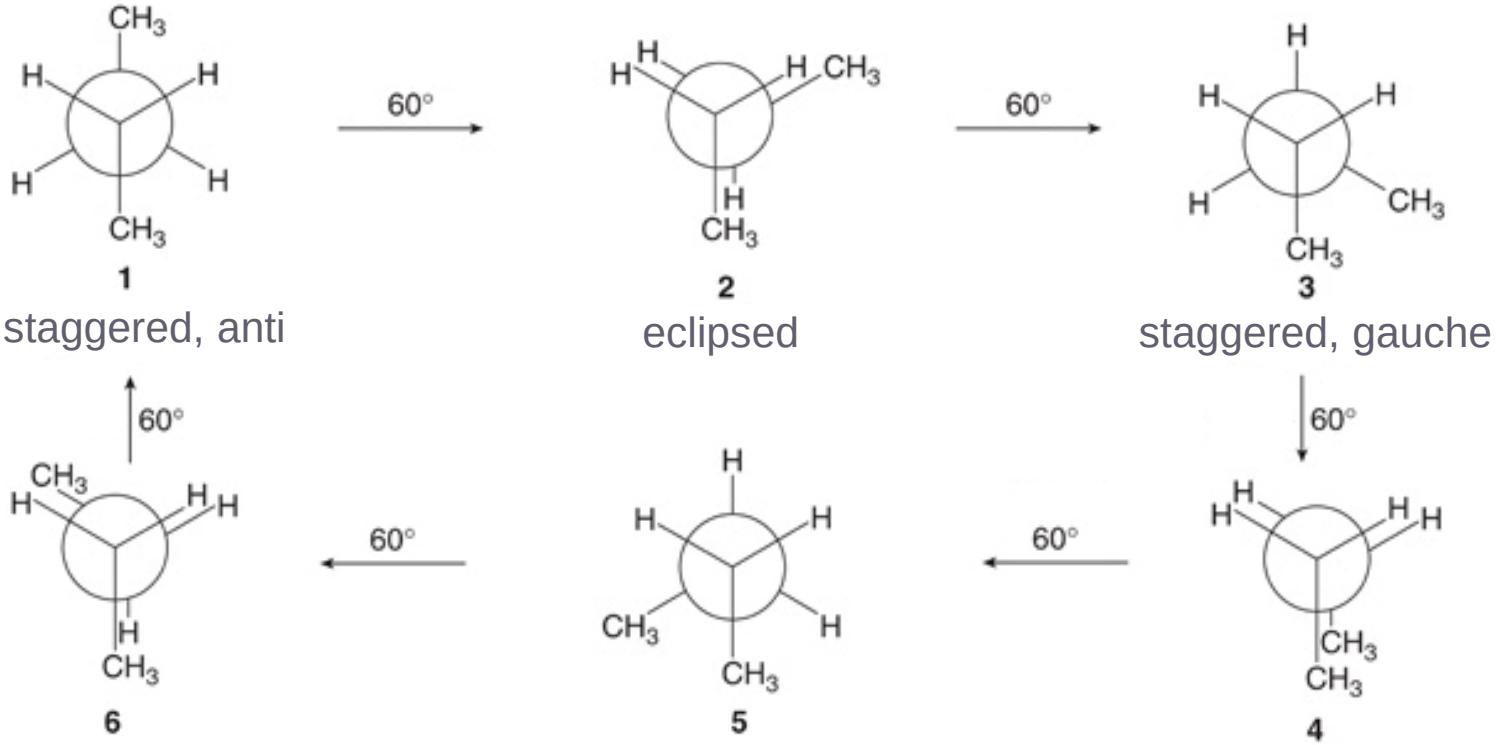


Torsional Strain (3.3 kcal/mole) is higher than in ethane. The methyl group is bulkier than a hydrogen atom

Conformations of Butane



6 different conformations



Conformations of Butane

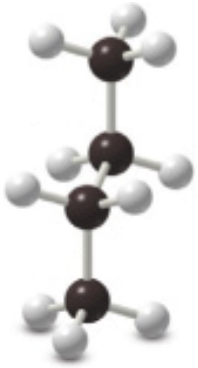
A staggered conformation with two large groups at 180° is called *anti*

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

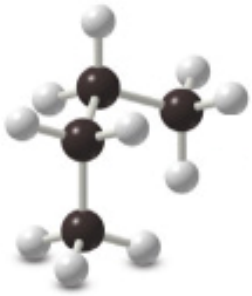
anti conformation

conformazione gauche

The CH_3 are at 180°



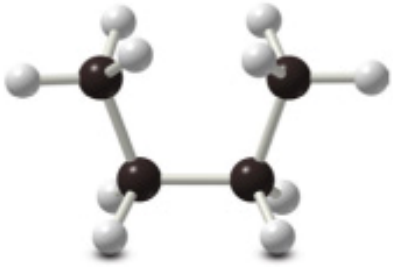
1



3

The CH_3 are at 60°
steric strain

Eclipsed conformation

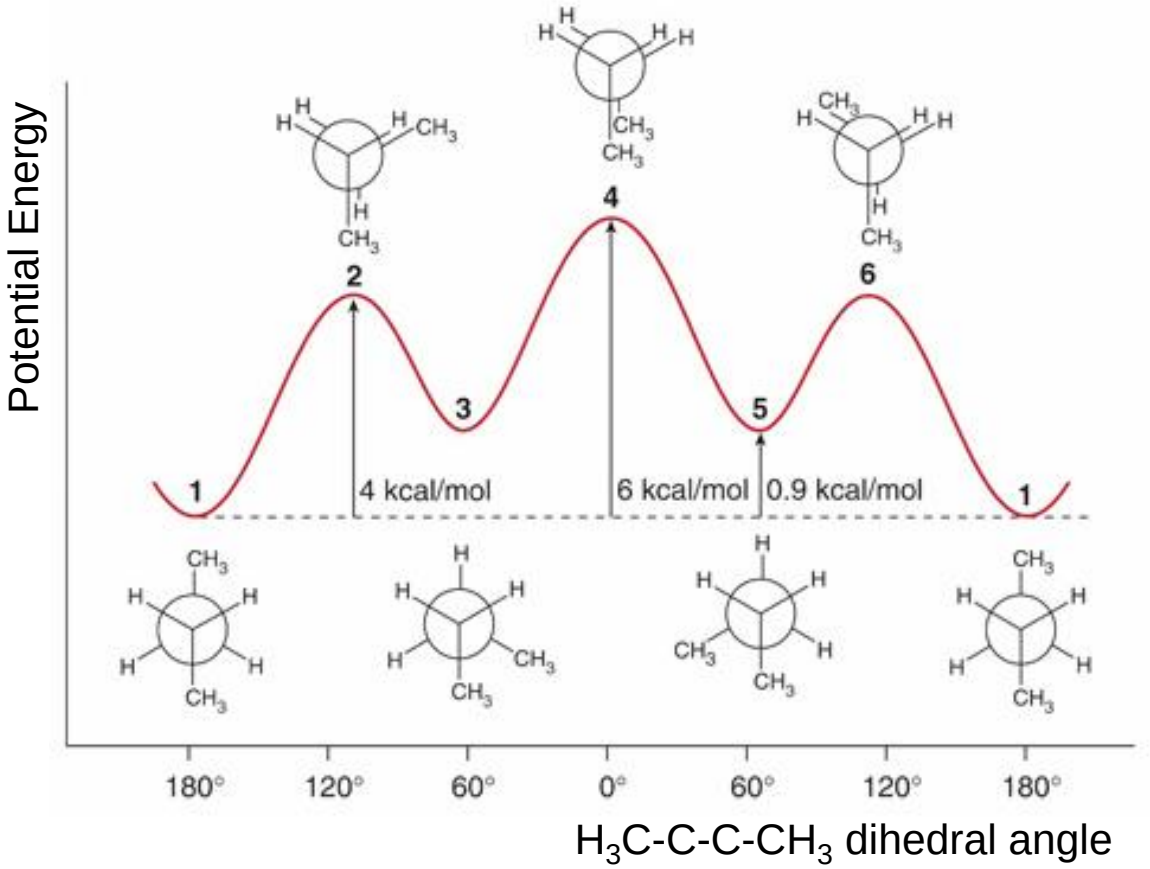


4

The CH_3 are at 0°
steric strain

Conformations of Butane

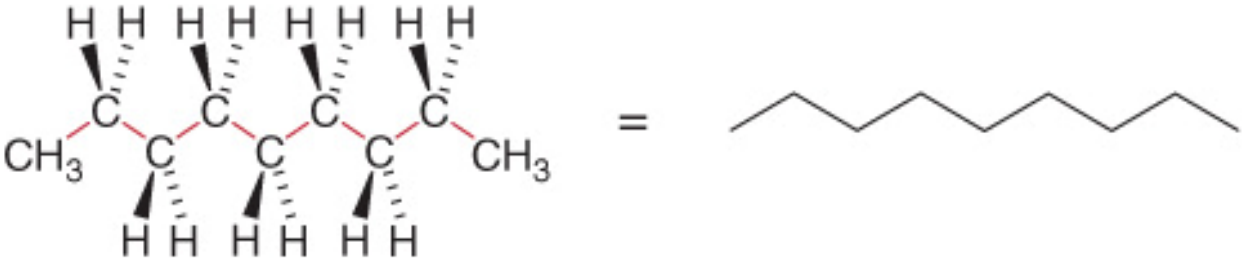
- *Staggered conformations*:
  - **1** (anti) is the absolute minimum
  - **3,5** (gauche) are relative minima
- *Eclipsed conformations:*
  - **4** is the absolute maximum (CH_3 eclipsed)
  - **2,6** are relative maxima



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.



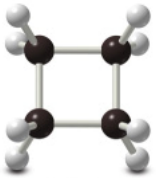
Cycloalkanes

Cycloalkanes

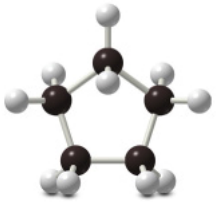
- Cycloalkanes have empirical formula $\mathbf{C_nH_{2n}}$ and contain carbon atoms arranged in a cyclic chain

- Nomenclature: cyclo + name of the corresponding alkane

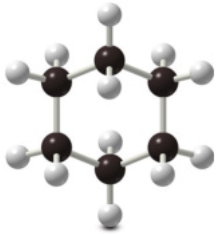
cyclopropane
C_3H_6



cyclobutane
C_4H_8



cyclopentane
C_5H_{10}

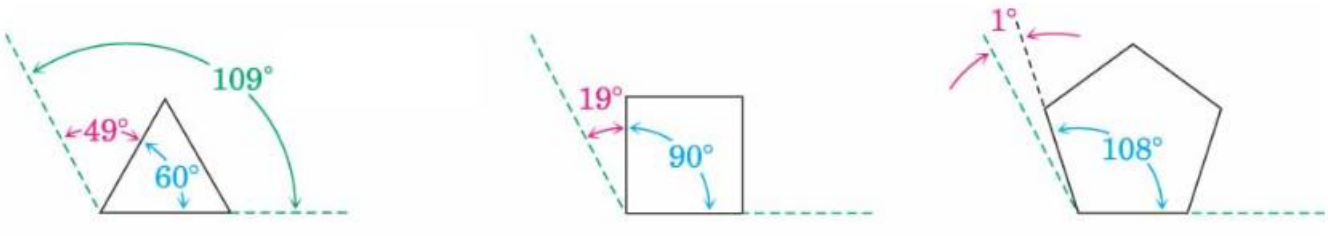


cyclohexane
C_6H_{12}

Stability: Angular Strain (Baeyer's Strain)

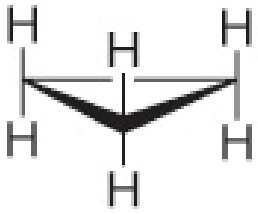
- Baeyer (1885): as carbon prefers 109° bond angles, rings other than five or six membered may be too strained to exist.

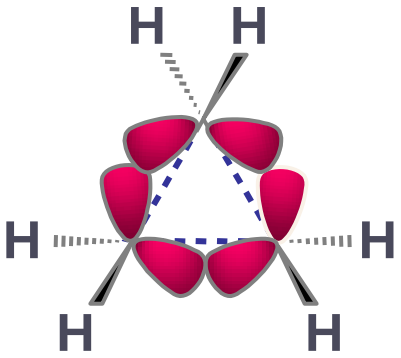
- Cycloalkanes from C_3 to C_{30} do exist, but some of them are strained because of distorted bond angles and other interactions.

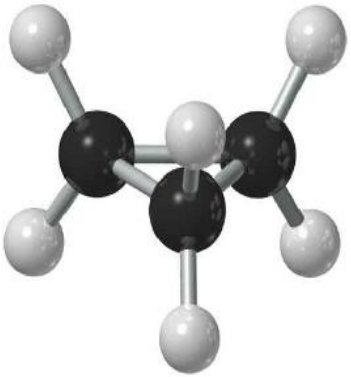


Cyclopropane C_3H_6

- Planar.
- Angle strain: 60° CCC angles.
- Torsional strain: all H are eclipsed.
- May be described as sp3 hybridized with banana bonds.

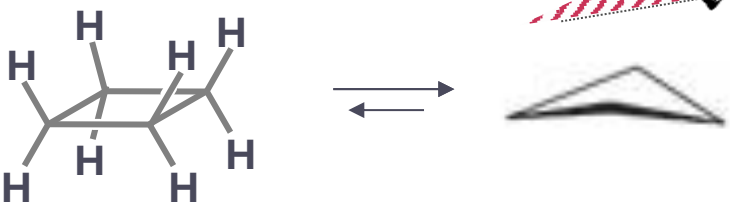






Cyclobutane C_4H_8

- 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

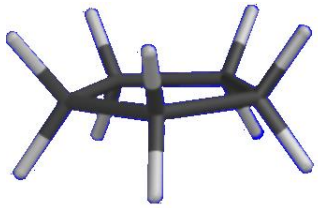
Puckered
slightly higher angle strain
lower torsional strain
some VdW strain

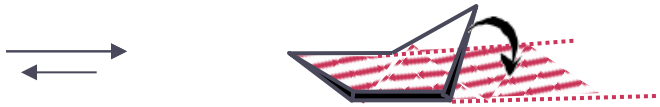
Ring Strain

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}

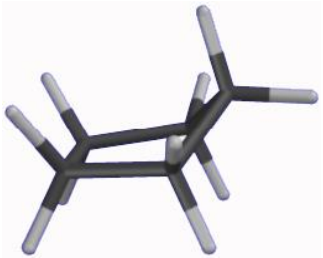


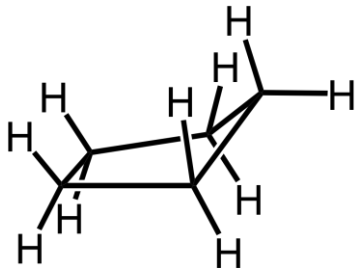


25°
puckering angle

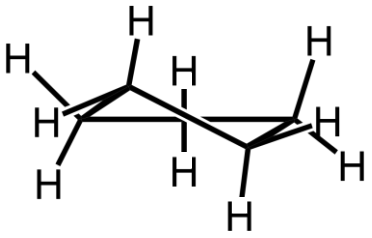
angle strain
torsional strain

"envelope" conformation
eclipsing is partially relieved

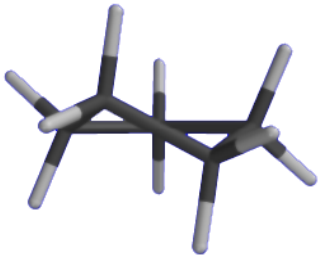




envelope



half-chair

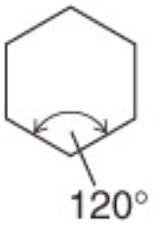


envelope and *half-chair* conformations have similar energies and rapidly interconvert into one another

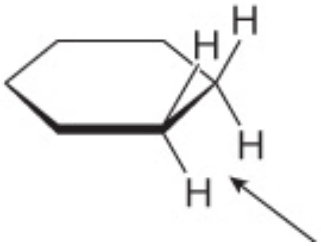
Cyclohexane C_6H_{12}

- Planar cyclohexane.

angle strain



CCC > 109.5°

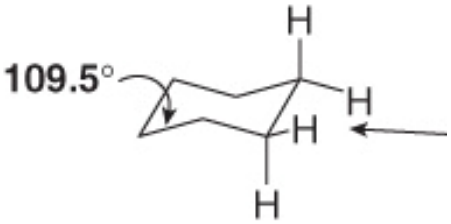


all H are eclipsed

torsional strain

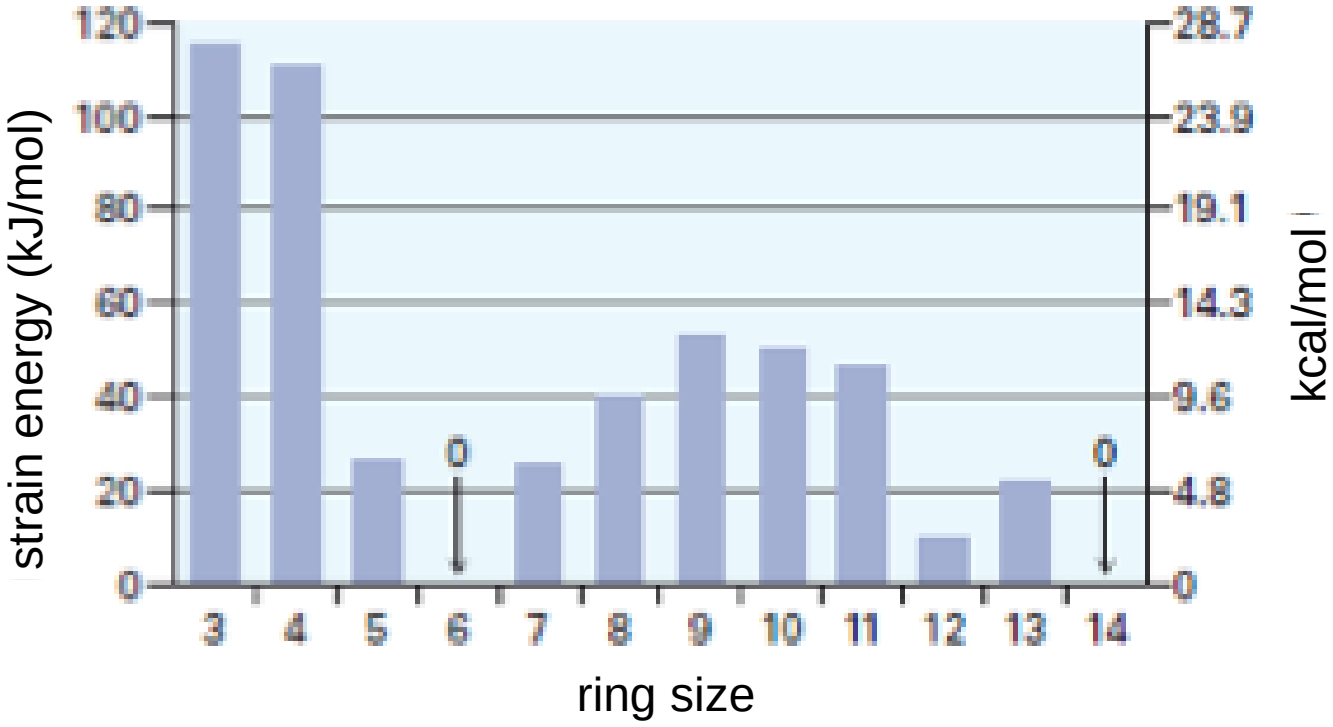
- *Chair* conformation.

strainless



H are staggered

Strain Energies of Cycloalkanes

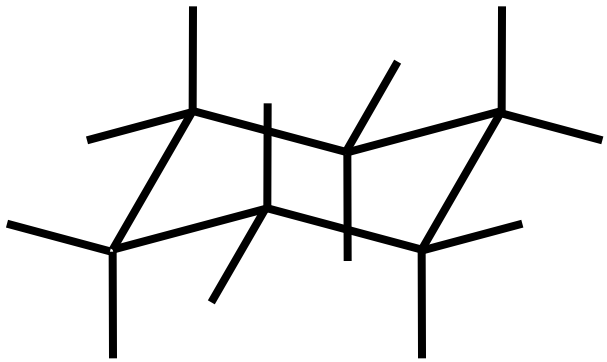


Strain Energies of Cycloalkanes

- 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).

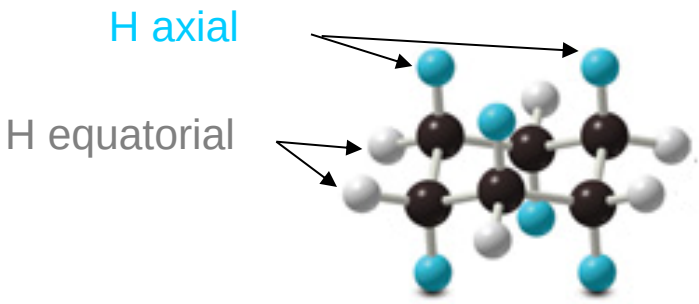
kJ/mol	2091	2724	3290	3910	4599	5264
Per CH_2	697	681	658	653	657	658
Strain	132	112	25	0	28	40

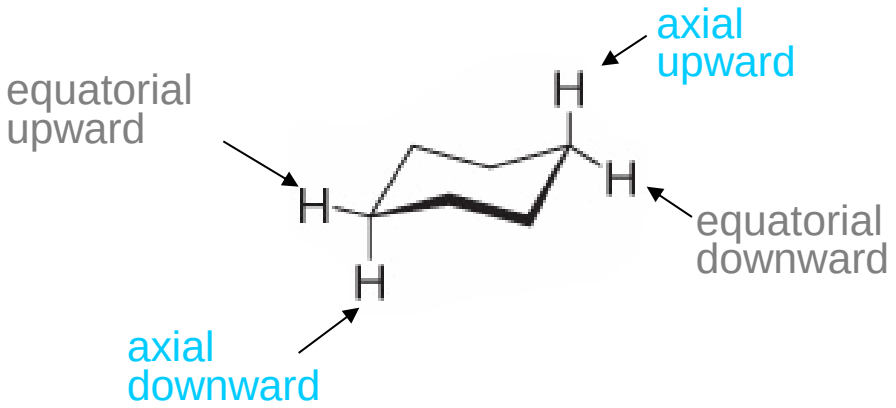
How to Draw Chair Cyclohexane



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.

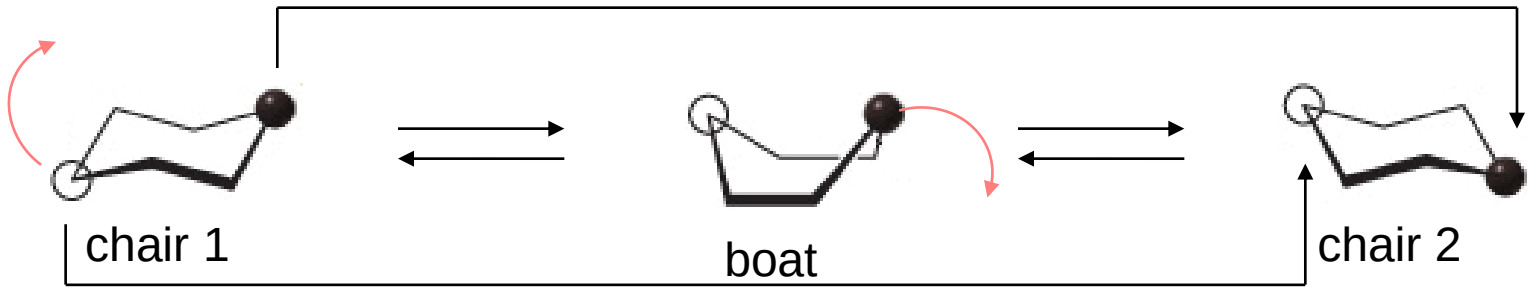




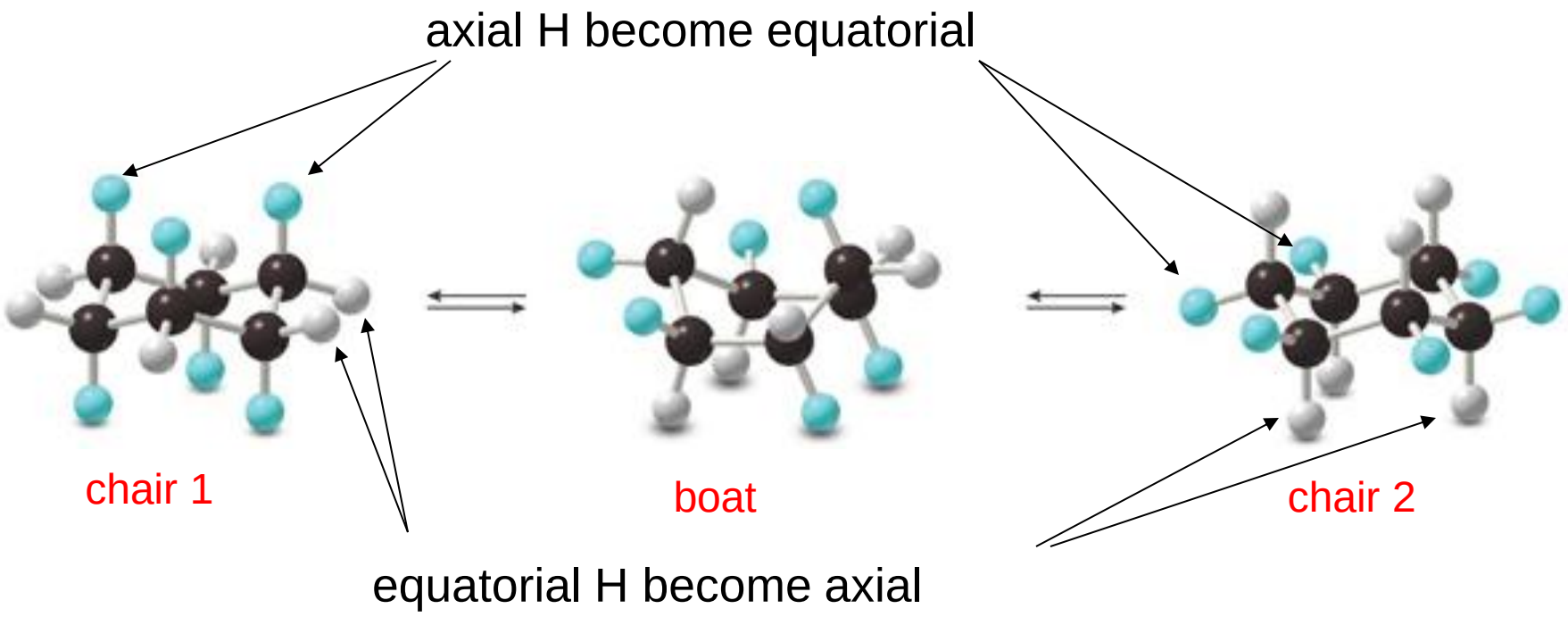
- There are 6 axial and 6 equatorial hydrogens in cyclohexane.

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.

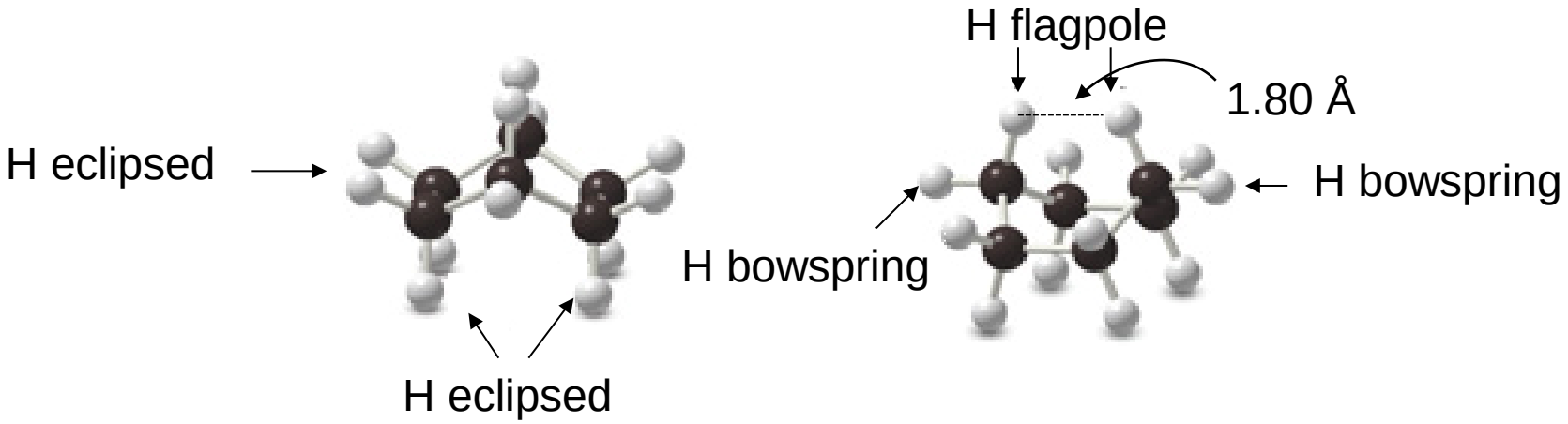


Ring Flipping

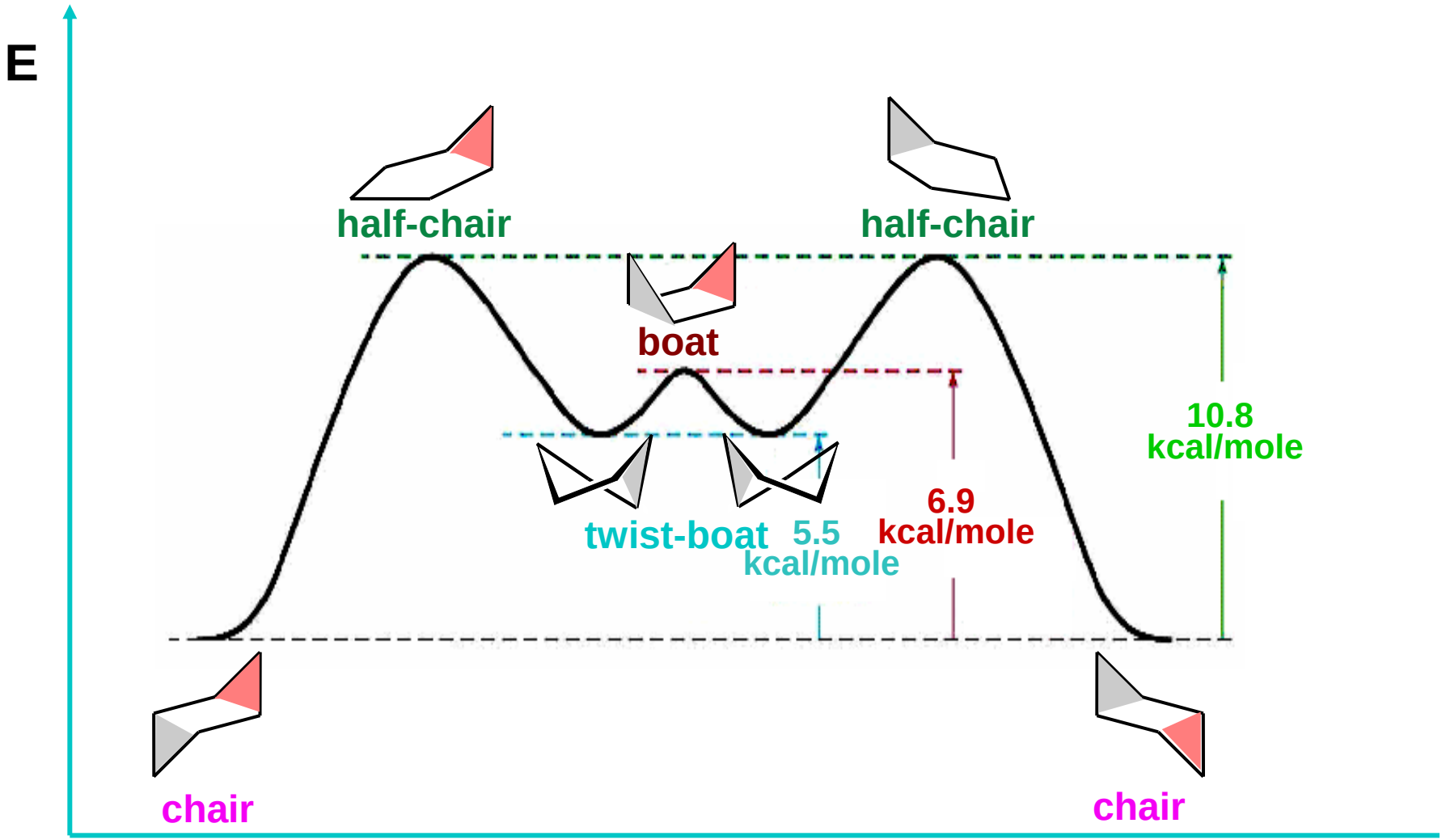


Conformations of Cyclohexane

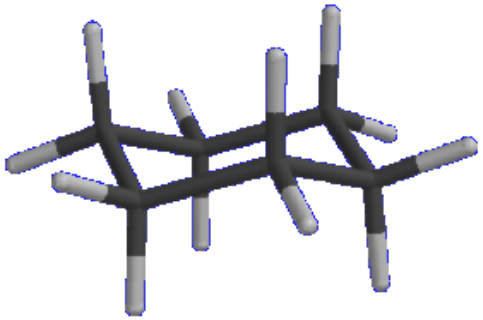
- Chair conformations are 7 kcal/mol more stable than boat conformations.
- Torsional strain. In the boat conformation the H on the base are eclipsed.
- Steric strain. Flag pole H are forced in close proximity.



Conformations of Cyclohexane



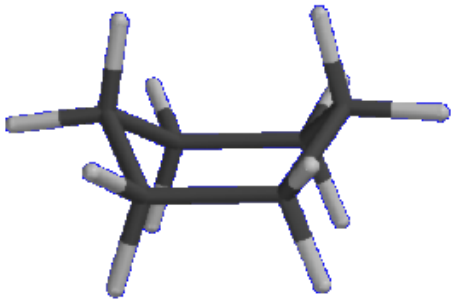
Conformations of Cyclohexane



chair

no ring strain

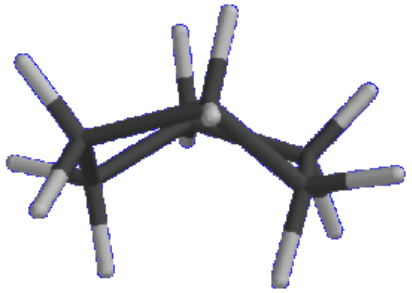
(99.99% at 25°C)



boat

- torsional strain
- steric strain

ring strain: ~ 7 kcal



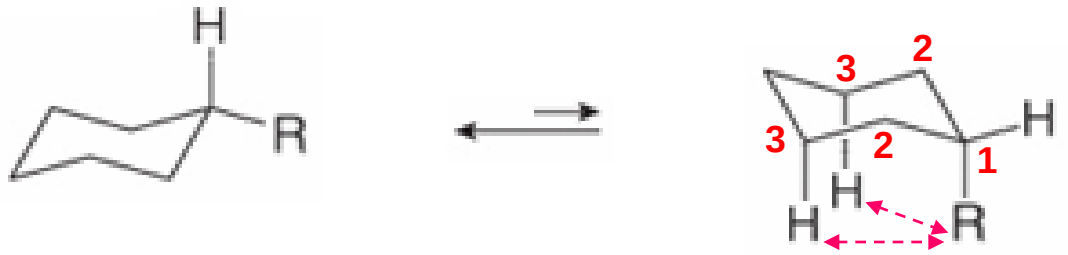
twist-boat

~ 1.5 kcal more stable than the boat

(0.01% at 25°C)

Substitued Cyclohexanes

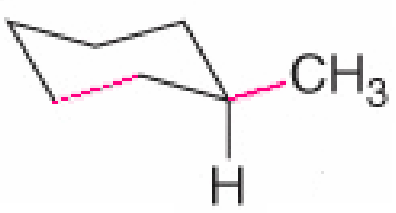
- The chair conformations are no longer equivalent: they have different energies.

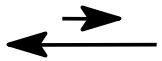


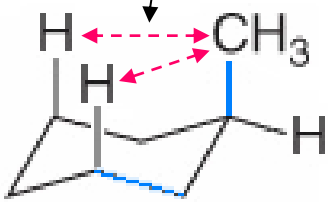
- The axial conformer is destabilized by 1,3-diaxial interactions (VdW interactions) between the substituent an axial hydrogens.
- The larger the substituent, the less stable the axial conformation.

Methylcyclohexane

equatorial
(95%)
no steric strain







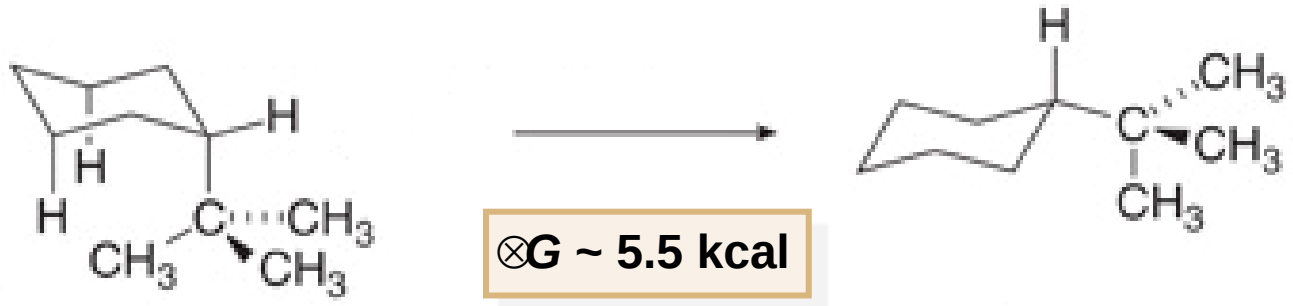
axial
(5%)
steric
repulsion

⊗***G*** **~ 1.8 kcal**

Each CH_3 / H interaction destabilizes the axial conformer by 0.9 kcal/mol

tert-Butylcyclohexane

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

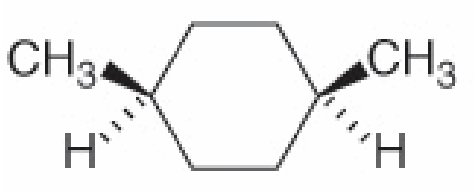


< 0.01% > 99.99%

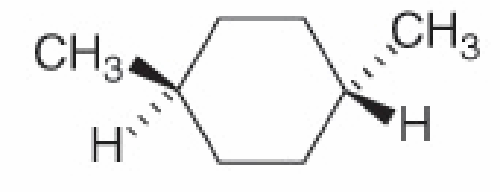
The *tert*-butyl group freezes the conformational equilibrium.

Disubstitued Cyclohexanes. Geometrical Stereoisomerism

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



cis

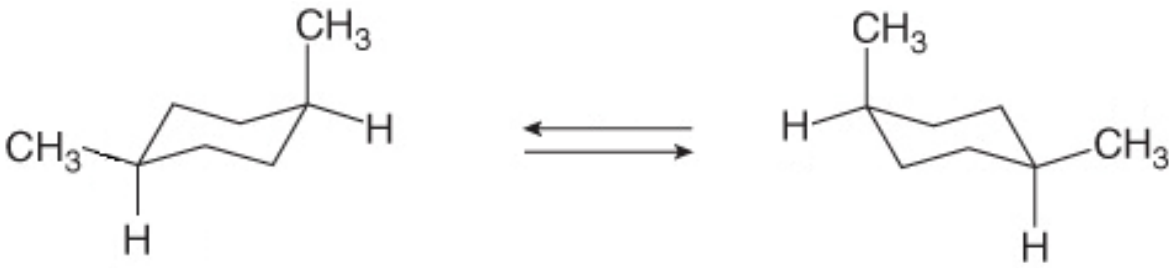


trans

- Each geometrical isomer has two possible chair conformations.

1,4-Dimethylcyclohexane

cis

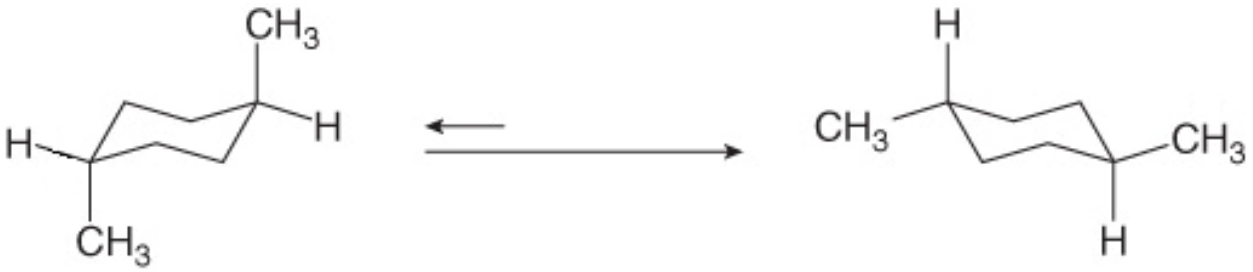


equatorial-axial
2 1,3-diaxial interactions
2 x 0.9 = 1.8 kcal

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

⊗*G* = 0 kcal

trans



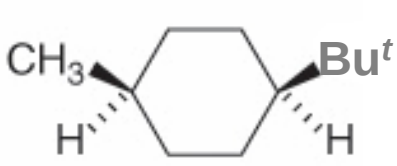
bisaxial
4 1,3-diaxial interactions
4 x 0.9 = 3.6 kcal

bisequatorial
no repulsions

⊗*G* ~ 3.6 kcal

cis-1-*t*-Butyl-4-methylcyclohexane

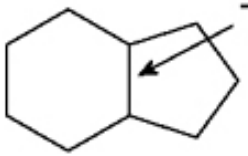
- The conformational equilibrium is frozen by the bulky t-butyl group.



5.5 kcal/mol 1.8 kcal/mole ⊗***G* ~ 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.

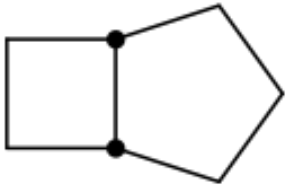
- Two non-adjacent atoms are shared by both rings.

A spiro bicyclic system

- One atom is shared by two rings

Polycyclic compounds

bicyclo[2.2.2]octane

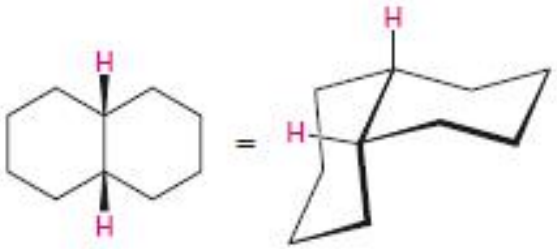


bicyclo[3.2.0]heptane

spiro[4,5]decane

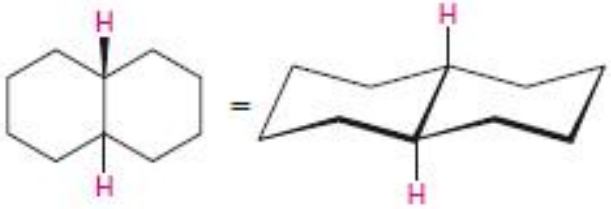
Polycyclic Hydrocarbons

less stable
(1 axial substituent)



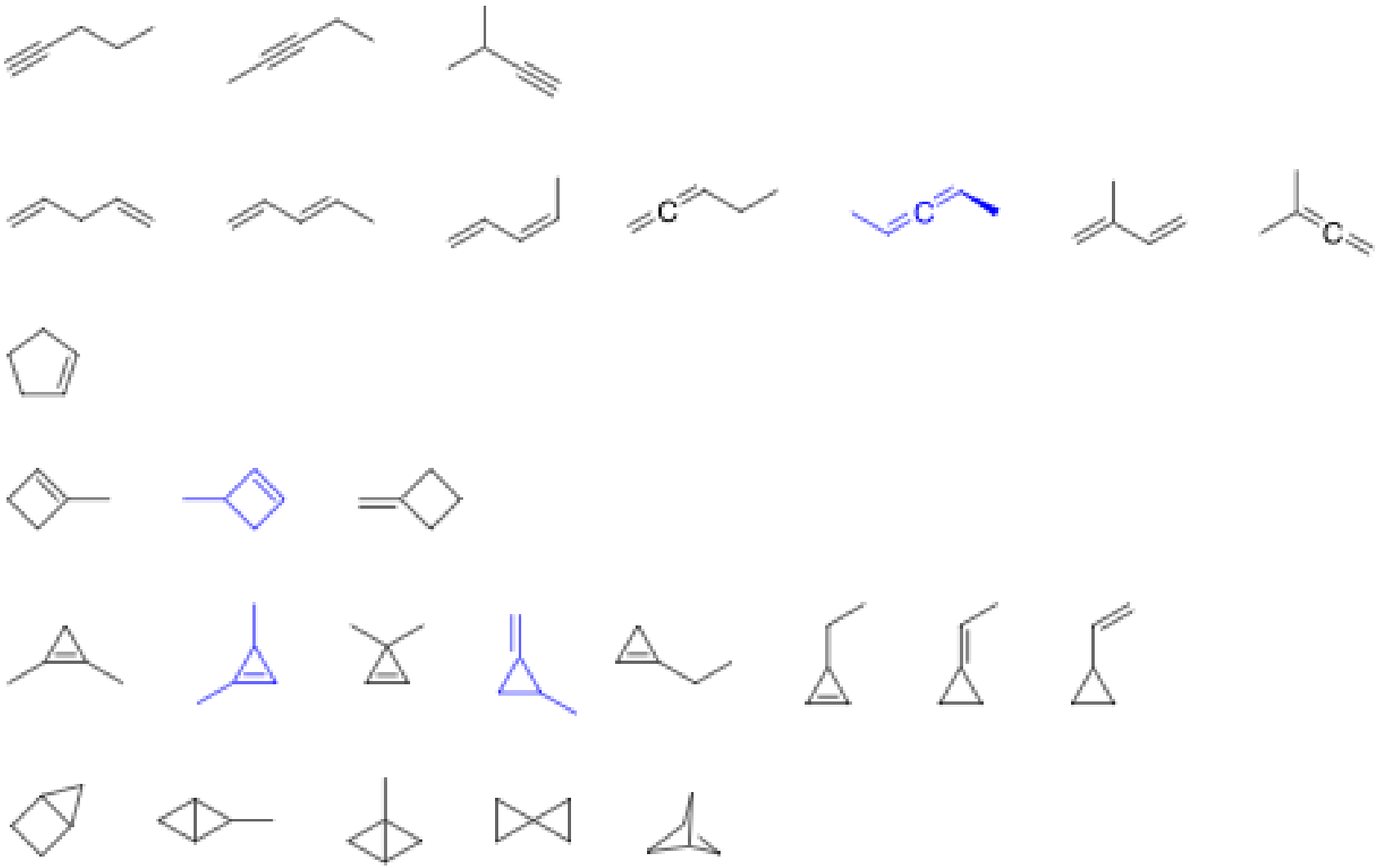
cis-decaline

more stable
(equatorial substituents)

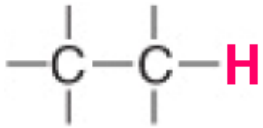


trans-decaline

C5H8 Isomers



Reactions of Alkanes



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

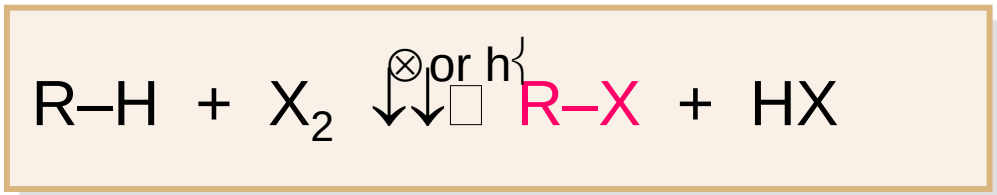
Alkanes react only at high temperatures, with radical mechanisms.

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.



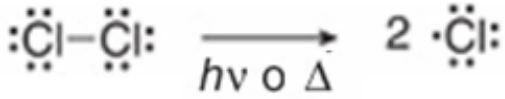
radical substitution

- 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

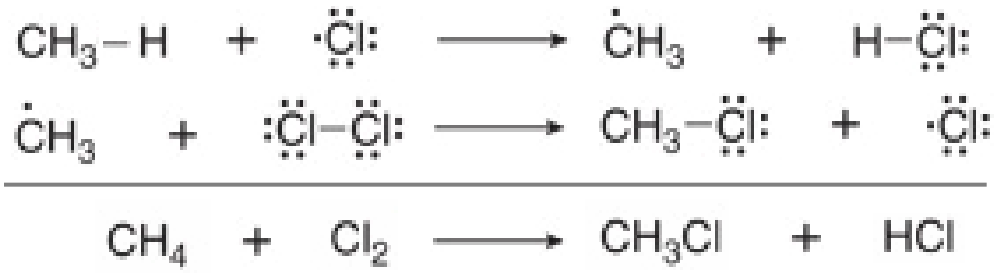
Initiation

Stage [1]: formation of Cl· radicals



Propagation

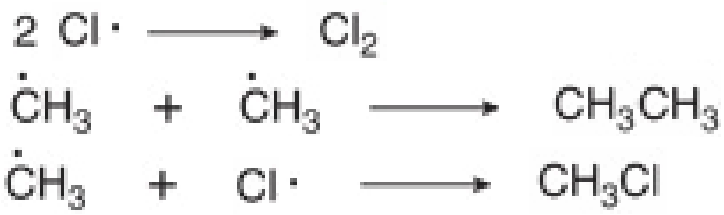
Stages [2] and [3]: A new radical is formed for each reacting radical



thousands of cycles. Chain reaction

Termination

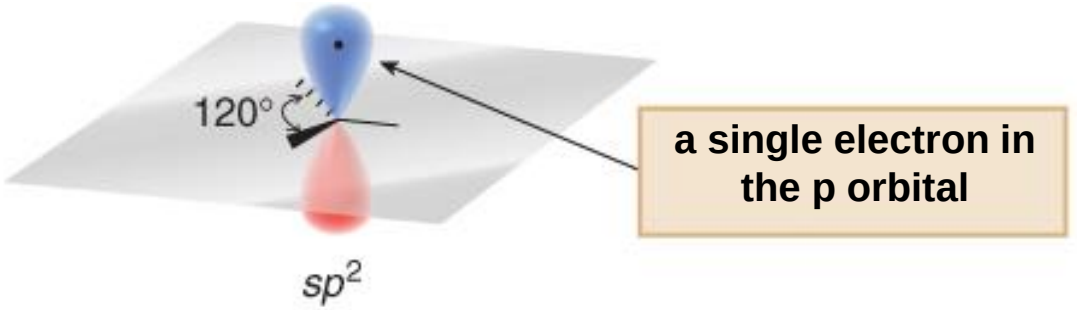
Stage [4]: Two radicals recombine forming a σ bond.



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	**1ry radical**	**2ry radical**	**3ry radical**



Energetics

Stage [2] is the slow step:

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

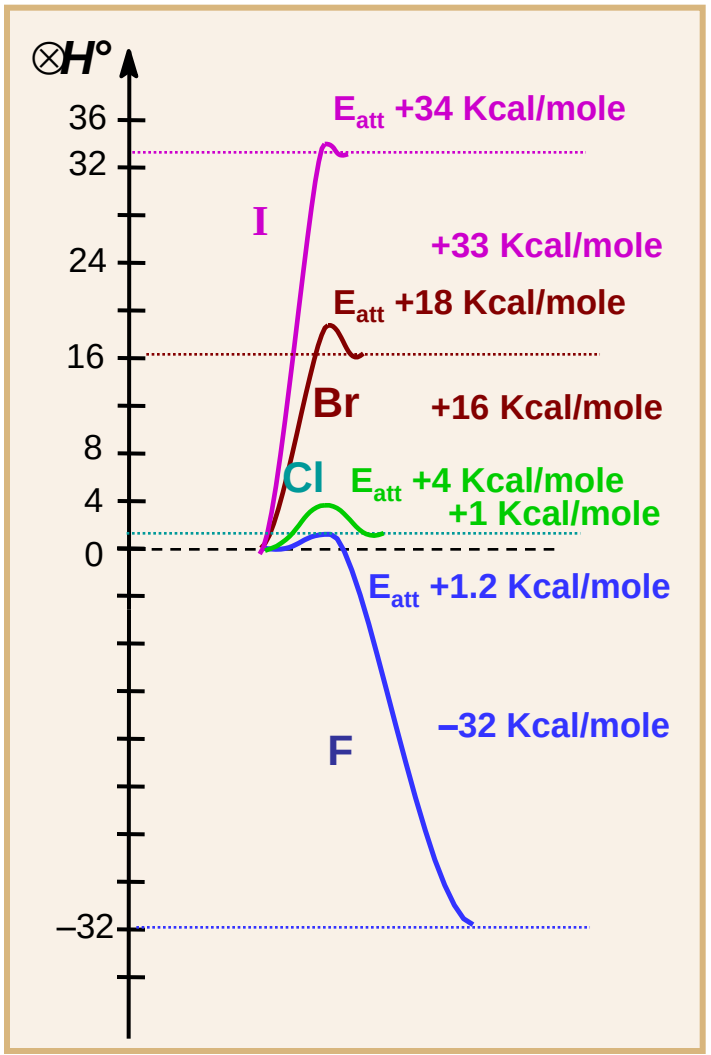
$\otimes H° = \otimes H°(C\text{-}H) - \otimes H°(X\text{-}H)$

$CH_4 \longrightarrow CH_4° + H°$ $\otimes H°(C\text{-}H)$

$H° + X° \longrightarrow H\text{-}X$ $- \otimes H°(X\text{-}H)$

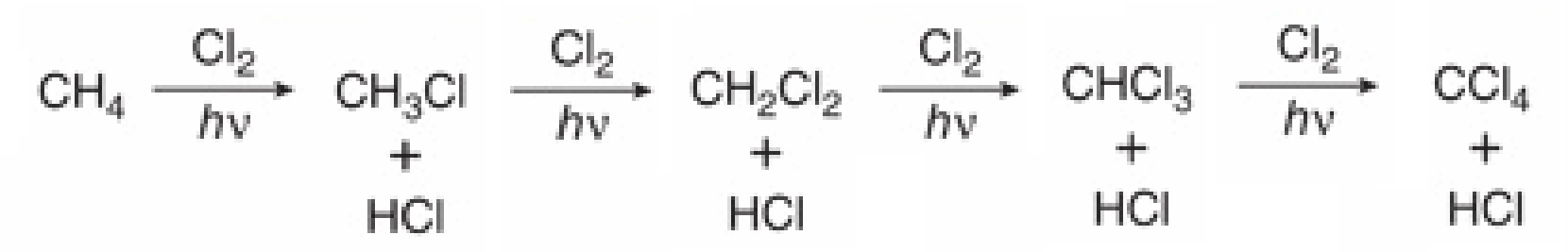
$\otimes H°$, Kcal/mole

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



Halogenation of Alkanes

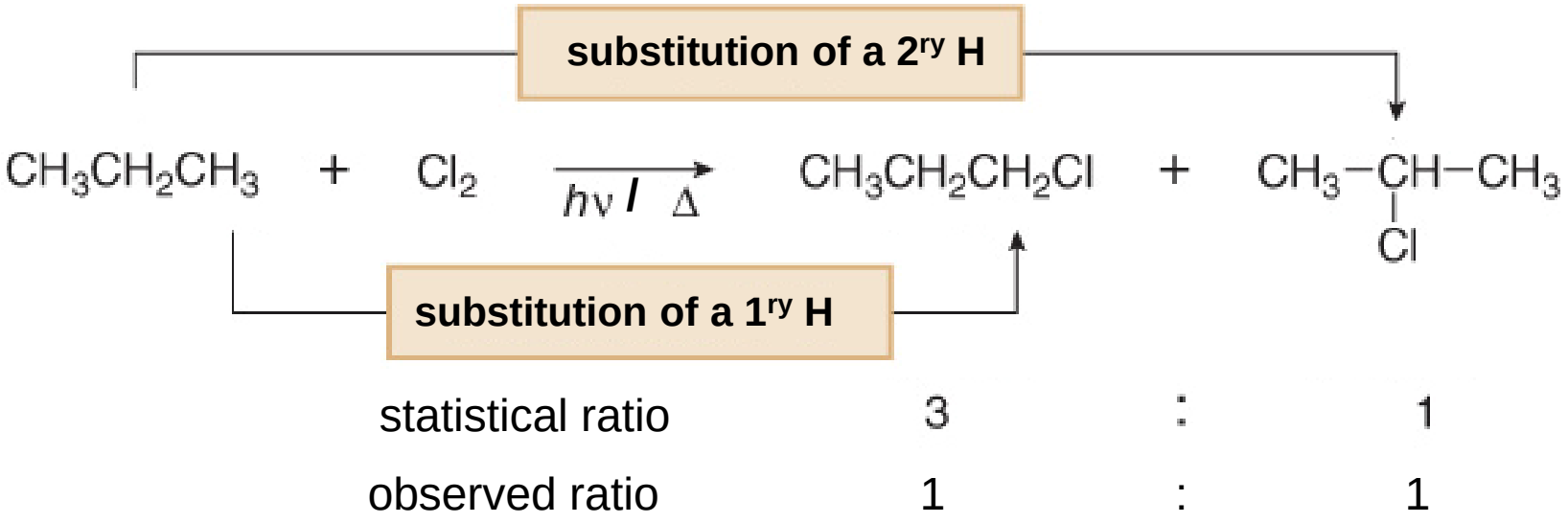
- Monohalogenation is only possible with an excess of substrate, otherwise polyhalogenation predominates.



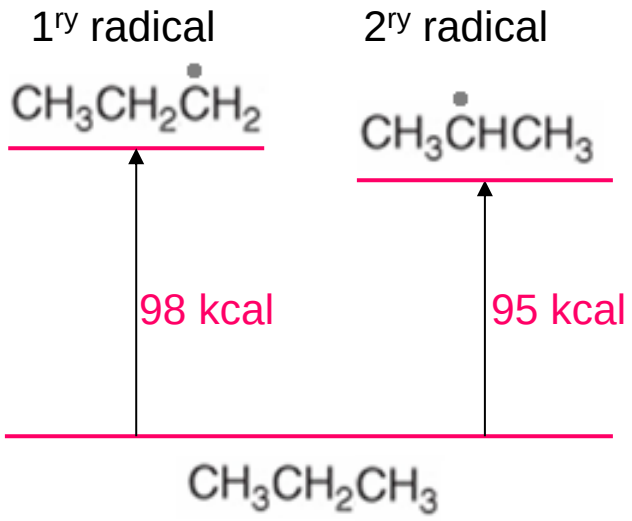
- Problem: mixture of halogenated products.
- Solution: CH_4 in large excess and recycled.

Regioselectivity

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



Regioselectivity



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

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

C−H Bond Dissociation Energies

R−H → R• + H•

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)**
$CH_3CH(H)CH_3$	**95 kcal/mole**	**(2^{ry} C-H)**
$CH_3C(CH_3)_2-H$	**91 kcal/mole**	**(3^{ry} C-H)**

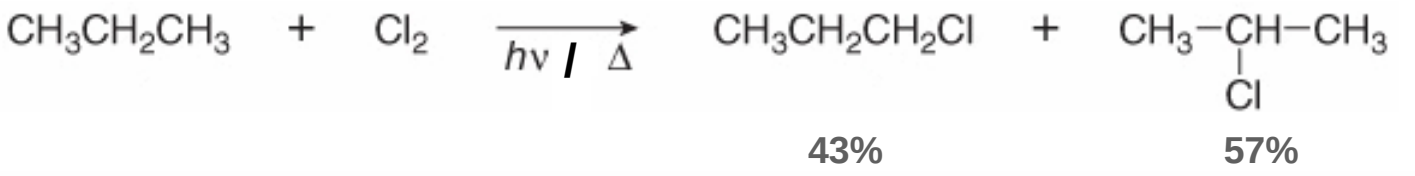
BDE ↑

REACTIVITY ↓

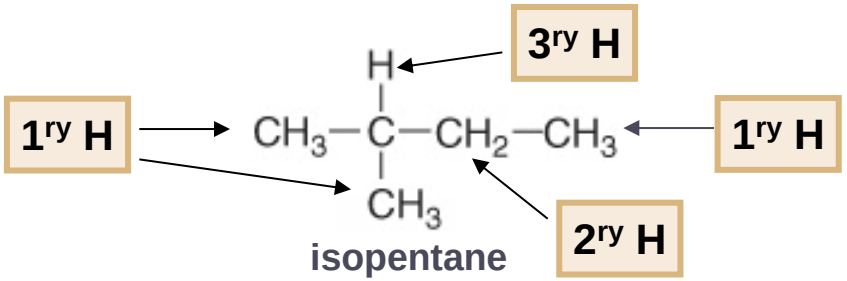
Reactivity of C−H bonds:
3^{ry} > 2^{ry} > 1^{ry} > CH_3−H

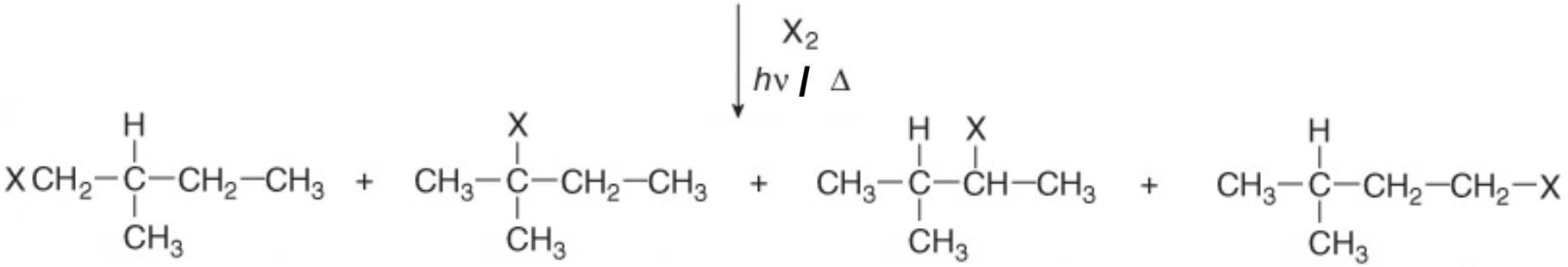
Reactivity and Selectivity

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



Regioselectivity



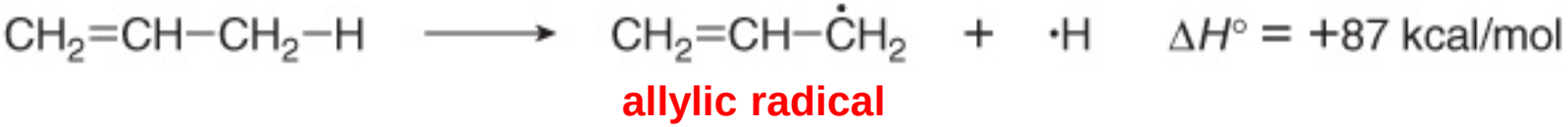


Cl_2:	28%	23%	35%	14%
Br_2:	~0%	90%	9%	~0%

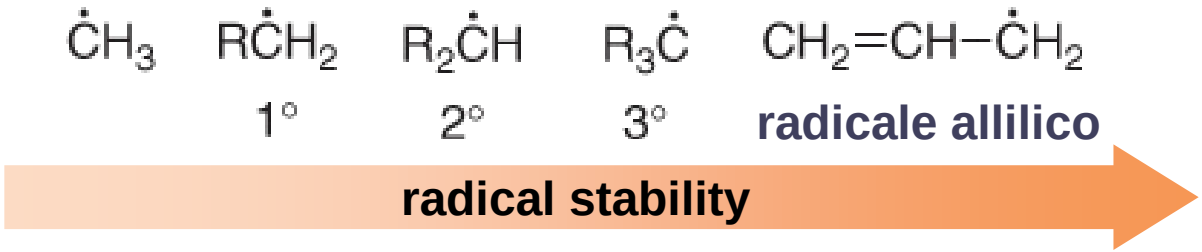
C-H relative reactivity	3ry	2ry	1ry
with Cl_2	5.2	3.9	1
with Br_2	1640	82	1

Halogenation of Allylic Carbons

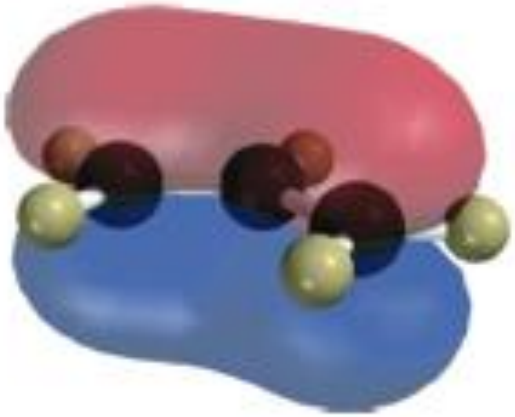
- Allylic carbons are sp^3 carbons adjacent to a double bond.
- A resonance-stabilized allylic radical is obtained by omolysis of an allylic C−H bond.



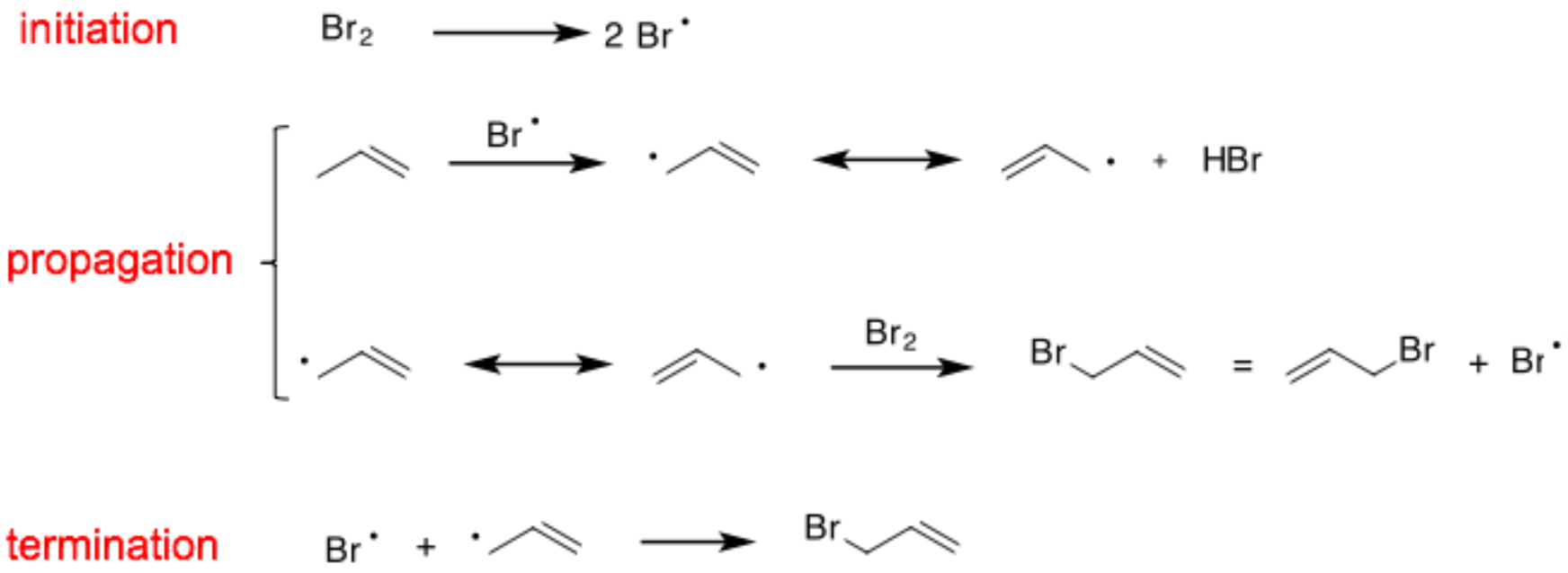
- BDEs of allylic C−H bonds are approximately 4 kcal/mol lower than BDE for 3ry C−H bonds.
- The delocalized allylic radical is more stable than a 3ry radical.



The Allylic Radical

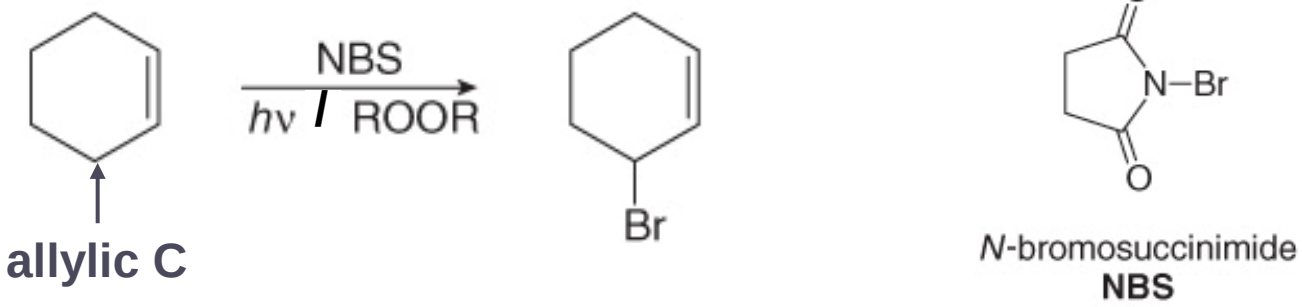


Halogenation of Allylic Carbons



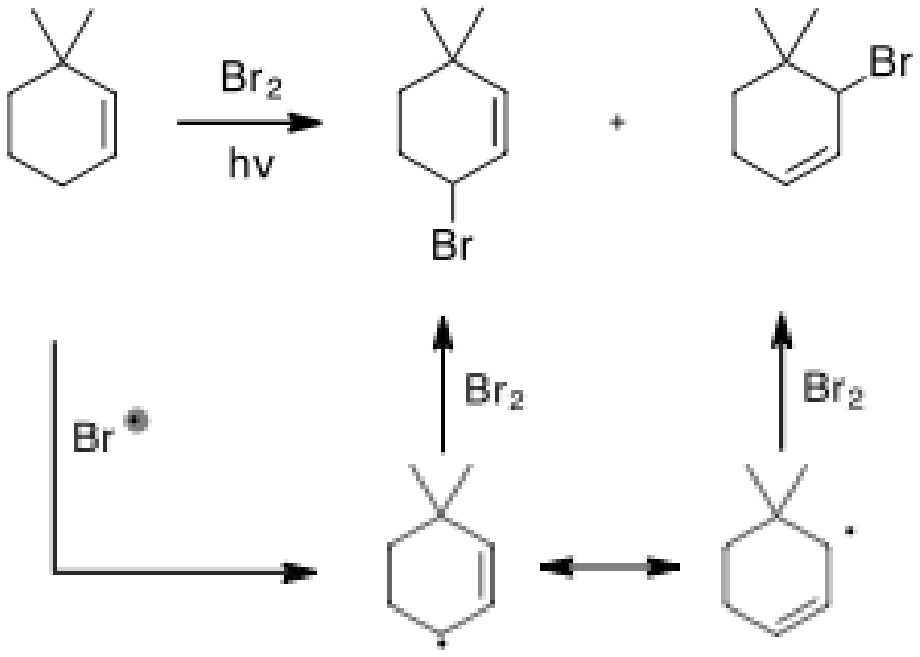
Halogenation of Allylic Carbons

- 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

- Combustion is a redox reaction. C is oxidized and O is reduced.
- All hydrocarbons burn giving carbon dioxide, water and heat ($\otimes H < 0$).
- 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

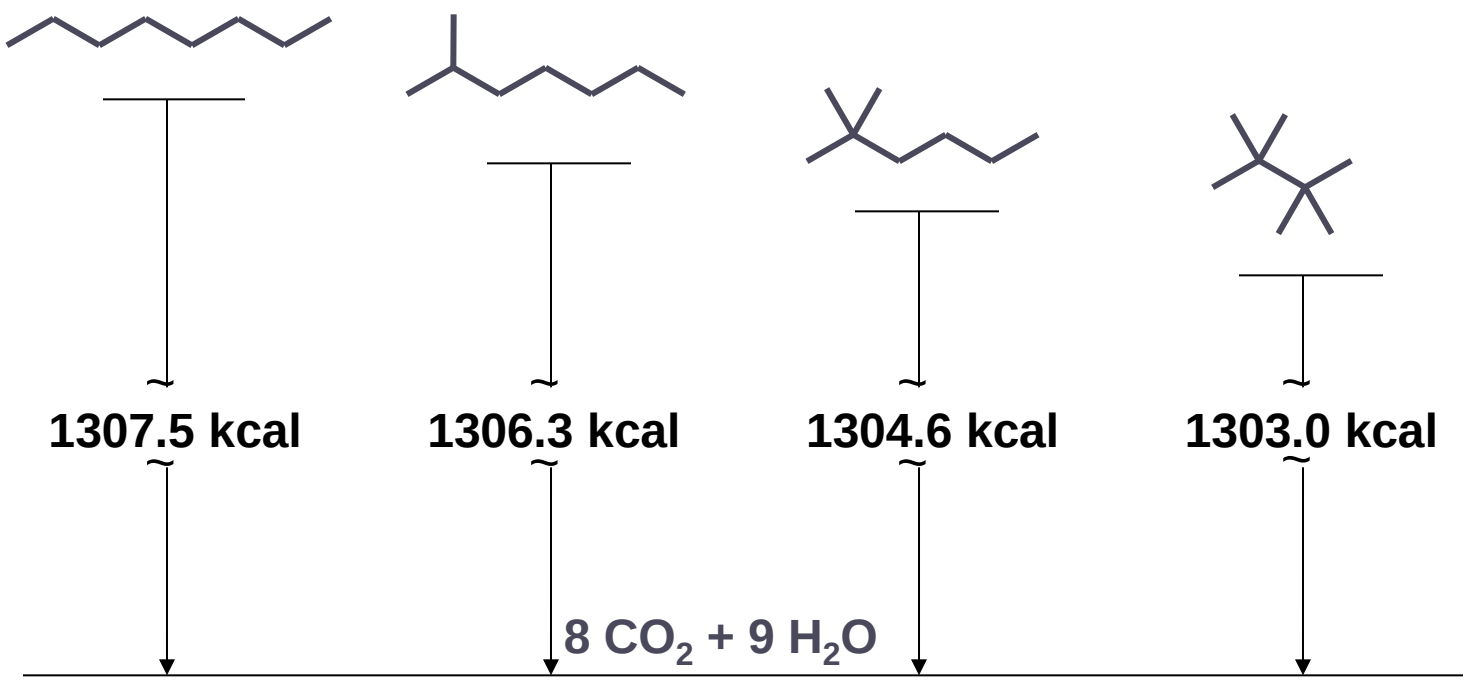
Strain Energies of Cycloalkanes

- 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

Stability of Isomers

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



Branched isomers are more stable than linear ones.