

Organic compounds

In the past, chemical compounds were divided into two large groups, inorganic and organic, based on their origin. Organic chemistry thus became the chemistry of carbon compounds.

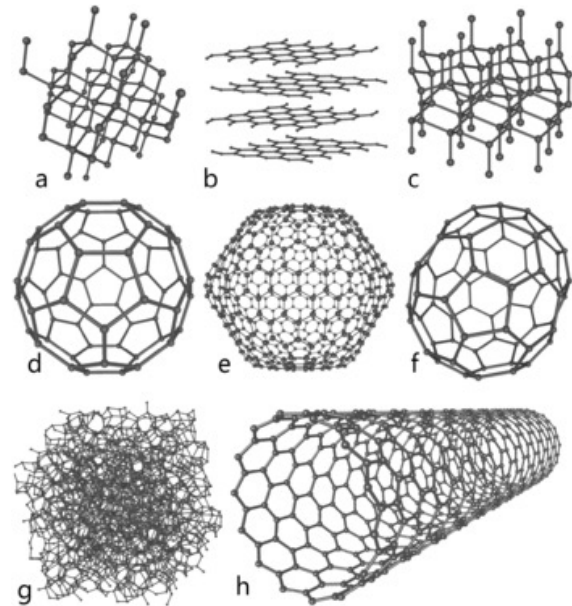
Maintaining the distinction was and is justified:

All organic compounds contain carbon.

- carbon compounds are much more numerous than the compounds of all other elements put together
- carbon has a special reactivity thanks to its electronic configuration

Il carbonio: il “lego” atomico.

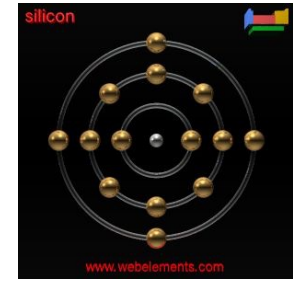
1. Carbon may form long covalent chains giving rise to many different compounds.
2. Carbon can form single, double, and triple bonds .
3. Carbon can form strong, stable bonds with H, O, S, P, N and with halogens.



Allotropic forms of Carbon



Carbon life vs silicon life



- Carbon forms C-C more stable than Si-Si ones (356 kJ/mol vs 230 kJ/mol)
- The oxidation product of silicon SiO_2 is a solid, Whereas CO_2 is a gas.



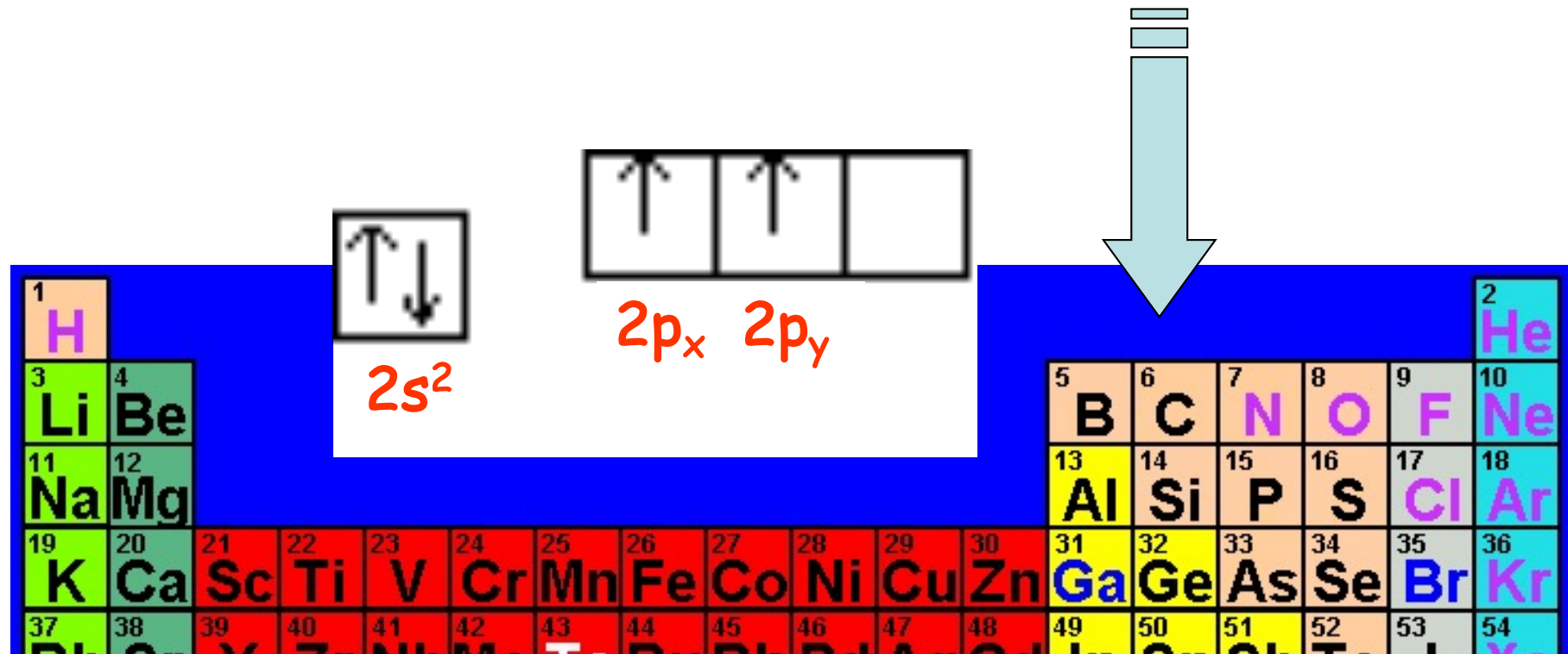
- Carbon forms chiral compounds, at difference with silicon.

Silicon life, “A Martian Odyssey” (S. Weisbaum)

Those bricks were its waste matter... We're carbon, and our waste is carbon dioxide, and this thing is silicon, and its waste is silicon dioxide-silica. But silica is a solid, hence the bricks. And it build itself in, and when it is covered, it moves over to a fresh place to start over.



ELECTRONIC STRUCTURE OF CARBON



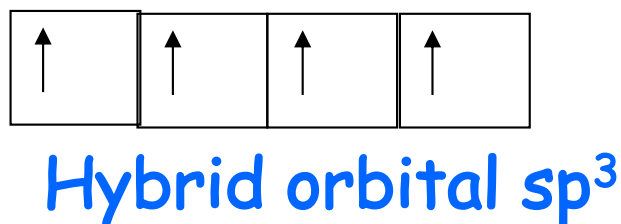
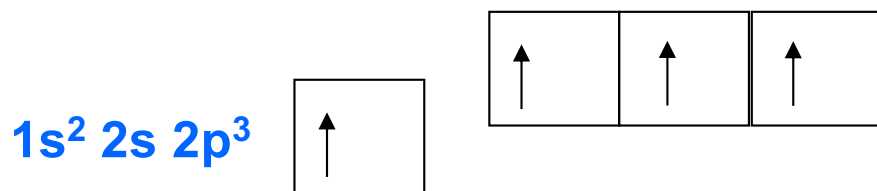
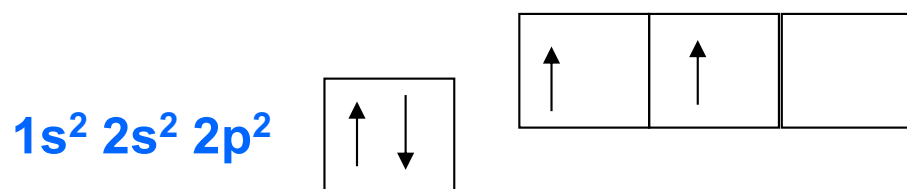
Carbon has electronic configuration $1s^2 2s^2 2p^2$

87	88	89	104	105	106	107	108	109	110										
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun										
58	59	60	61	62	63	64	65	66	67	68	69	70	71						
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu						
90	91	92	93	94	95	96	97	98	99	100	101	102	103						
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr						

With few exceptions (such as CO), carbon always forms 4 bonds.

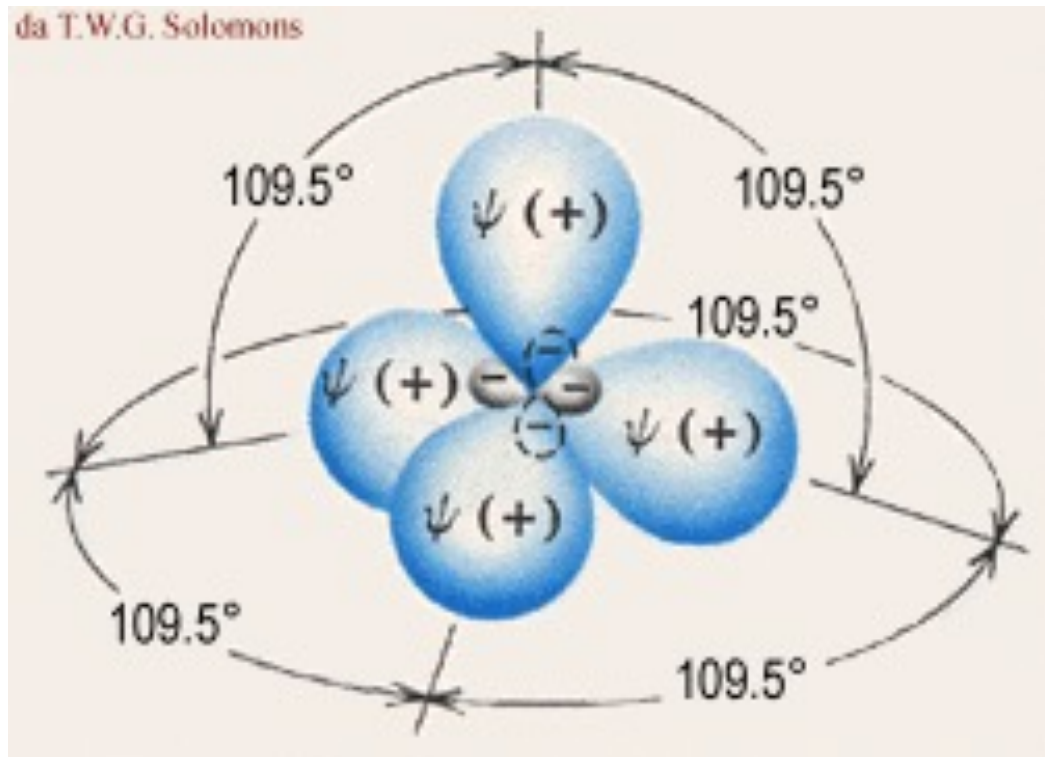


Ibridization: with a modest energy cost (compensated by the formation of 4 bonds rather than 2) C can decouple the two electrons in the 2s orbital and promote one in the empty orbital 2p_z assuming a configuration: 1s² 2s 2p³.



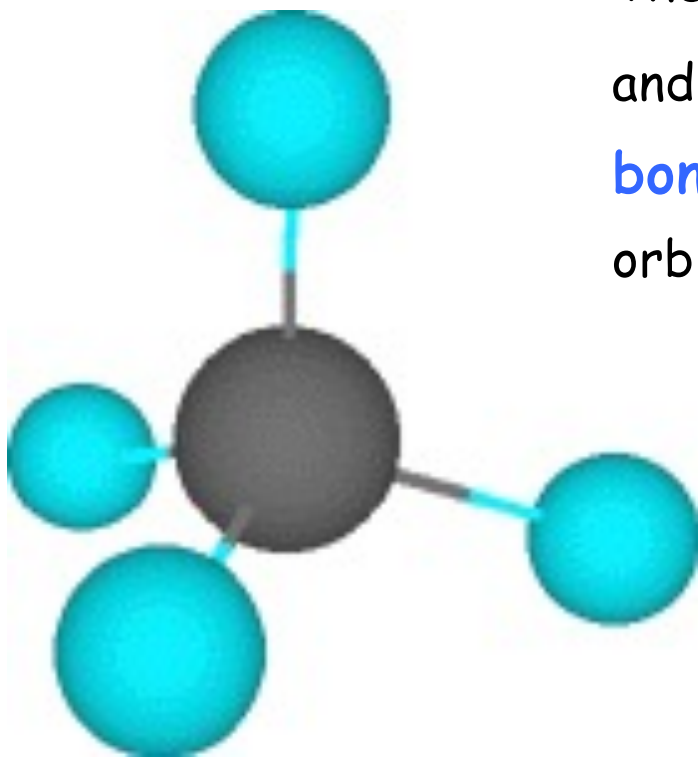
4 energetically
equivalent
orbitals

The 4 sp^3 hybrid orbitals are arranged to be as far as possible from each other, and are therefore oriented pointing to the four vertexes of a tetrahedron ($109^\circ 28'$).

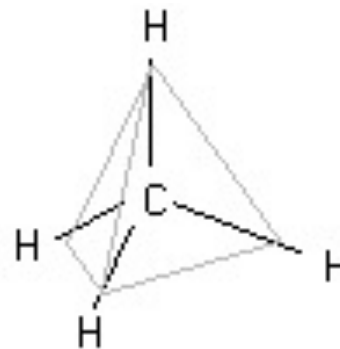
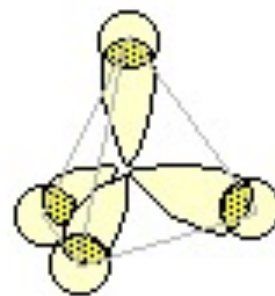


Ibridazione sp^3

Methane: CH₄

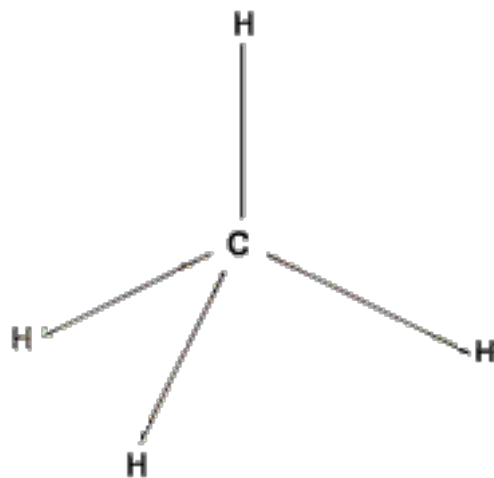


The bond arising from a carbon sp^3 electron and the hydrogen $1s$ electron is a σ bond (direction bond with maximum overlap of orbitals)

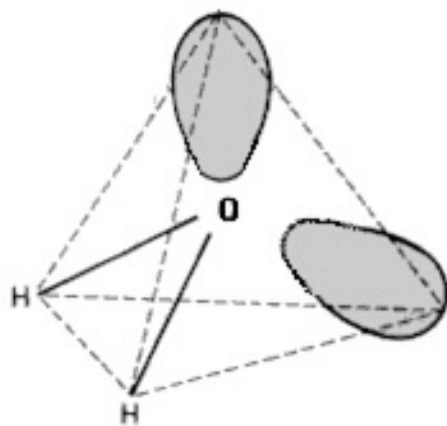


These are the bonds found in **ALKANES** where carbon forms 4 σ bonds with a tetrahedral geometry..

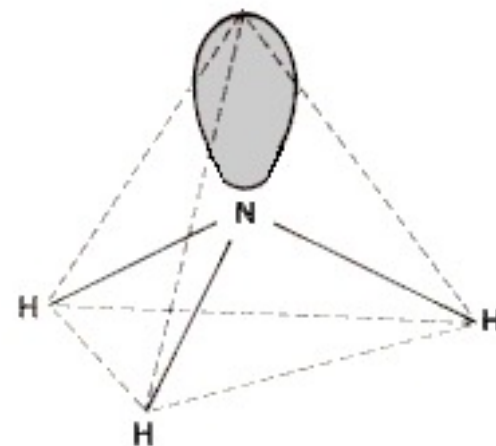
Tetrahedral geometries compared: sp^3 hybridization



Methane: CH₄

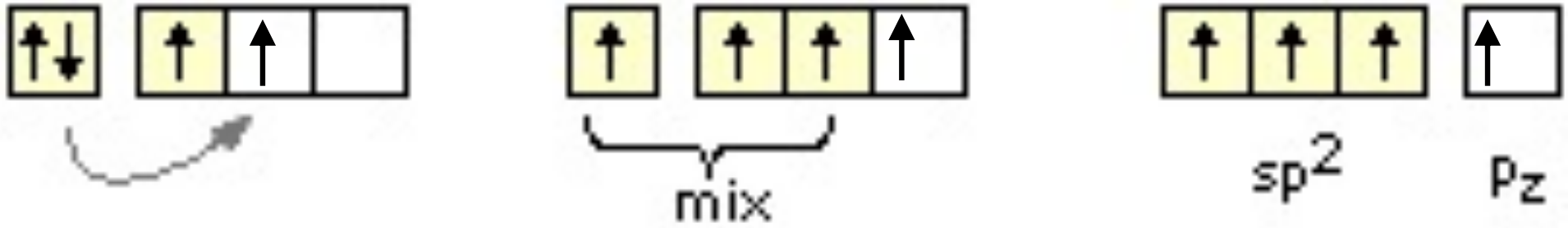


Water H₂O



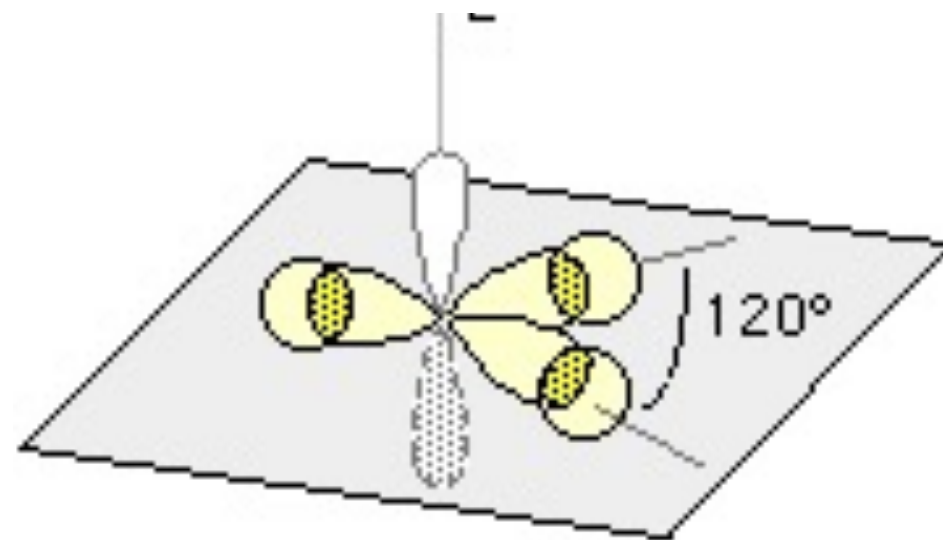
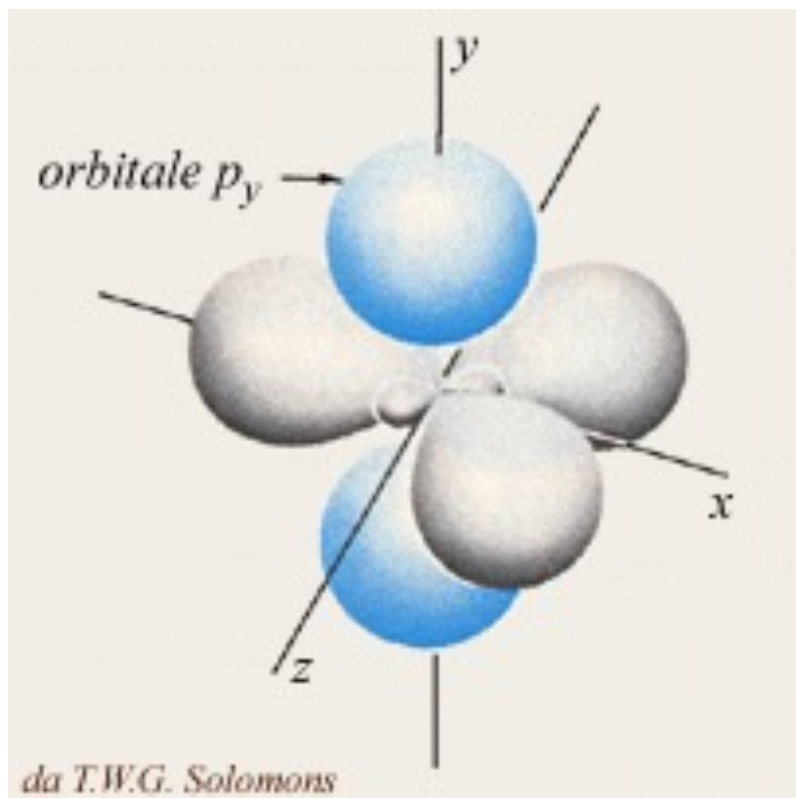
Ammonia NH₃

In sp^2 hybridization, orbitals $2s$, $2p_x$ e $2p_y$ are combined forming three equivalent orbitals



These orbitals lie on a plane with 120° angles. The geometry is trigonal-planar.

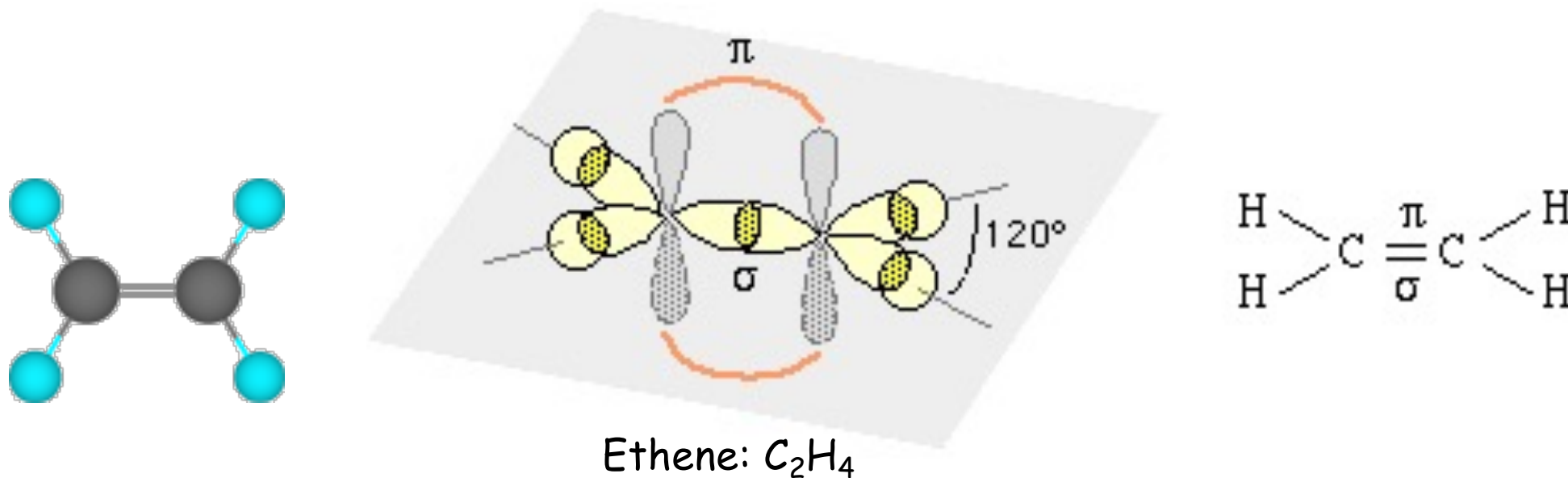
The $2p_z$ orbital which is not hybridized is orthogonal to the plane.



Sp^2 hybridization

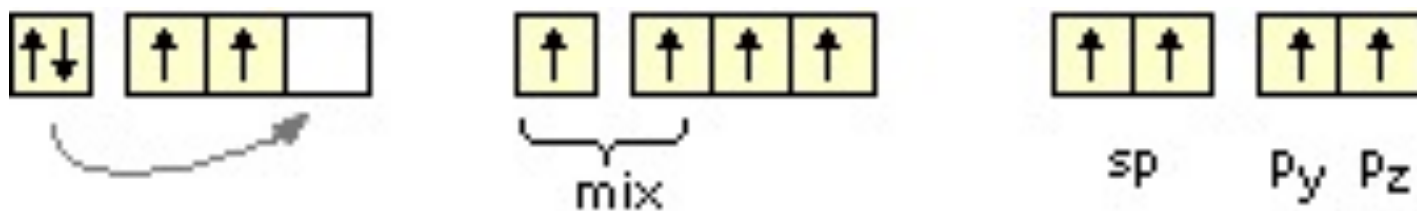
The 3 coplanar orbitals can form σ bonds, while the $2p_z$ one forms a π bond.

There can not be rotation around a π double bond, at difference with the σ .

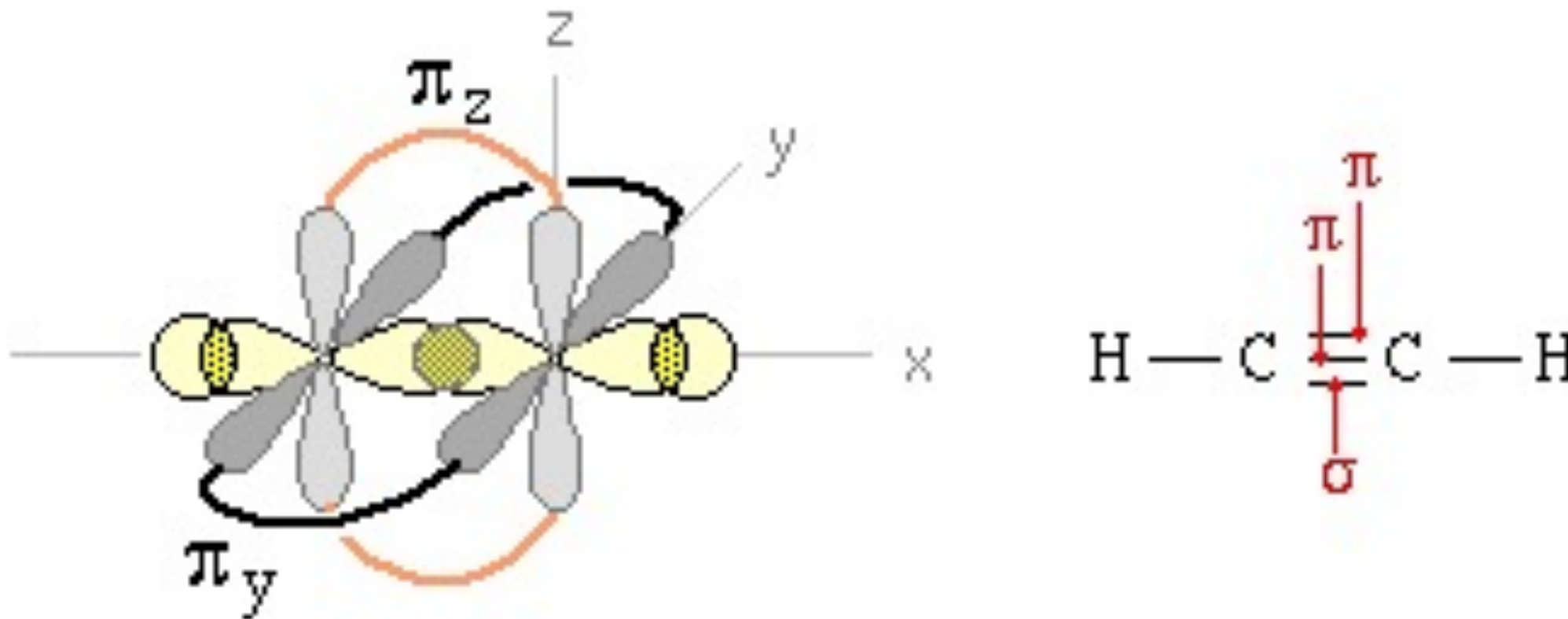


This is a characteristic of **ALKENES**, which are defined by having at least one double bond.

In the **sp hybridization** only $2s$ e $2p_x$ orbitals are combined, yielding 2 identical linear orbitals; the $2p_y$ e $2p_z$ orbitals are not modified. The hybrid sp orbitals form σ bonds (*linear geometri*, 180°), while the remaining nt hybridized ones can form π bonds.



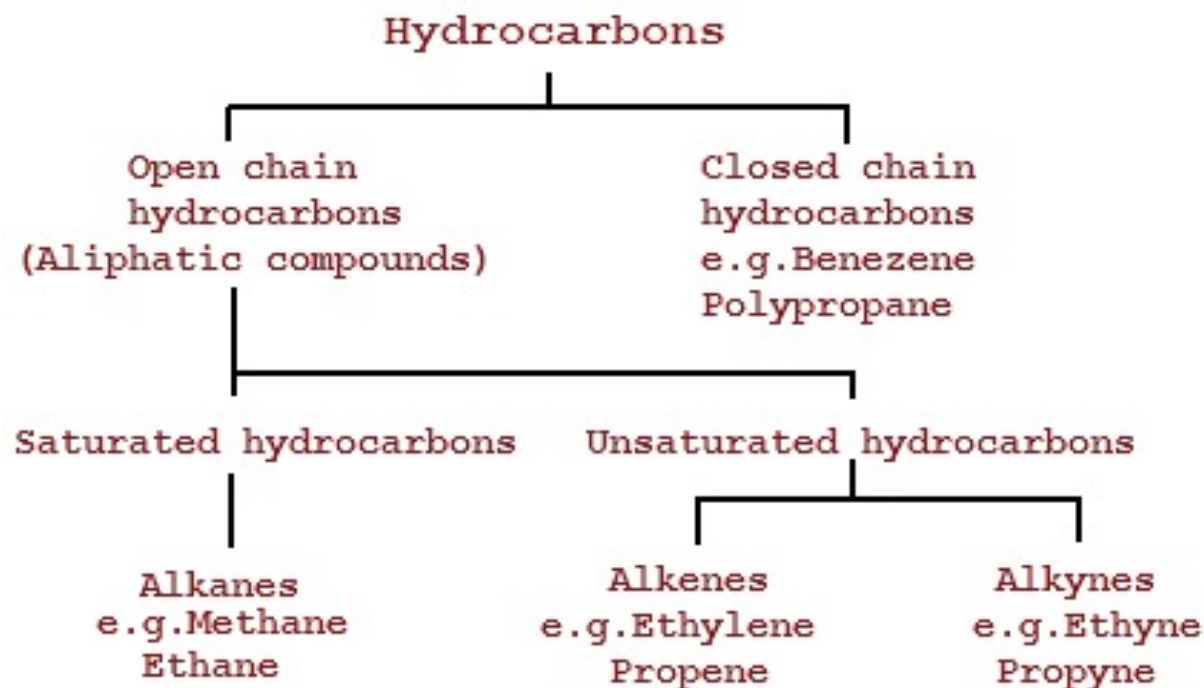
The sp hybridization is found in compounds that form triple C-C bonds (**ALKYNES**).



Ethyne (acetylene): C_2H_2

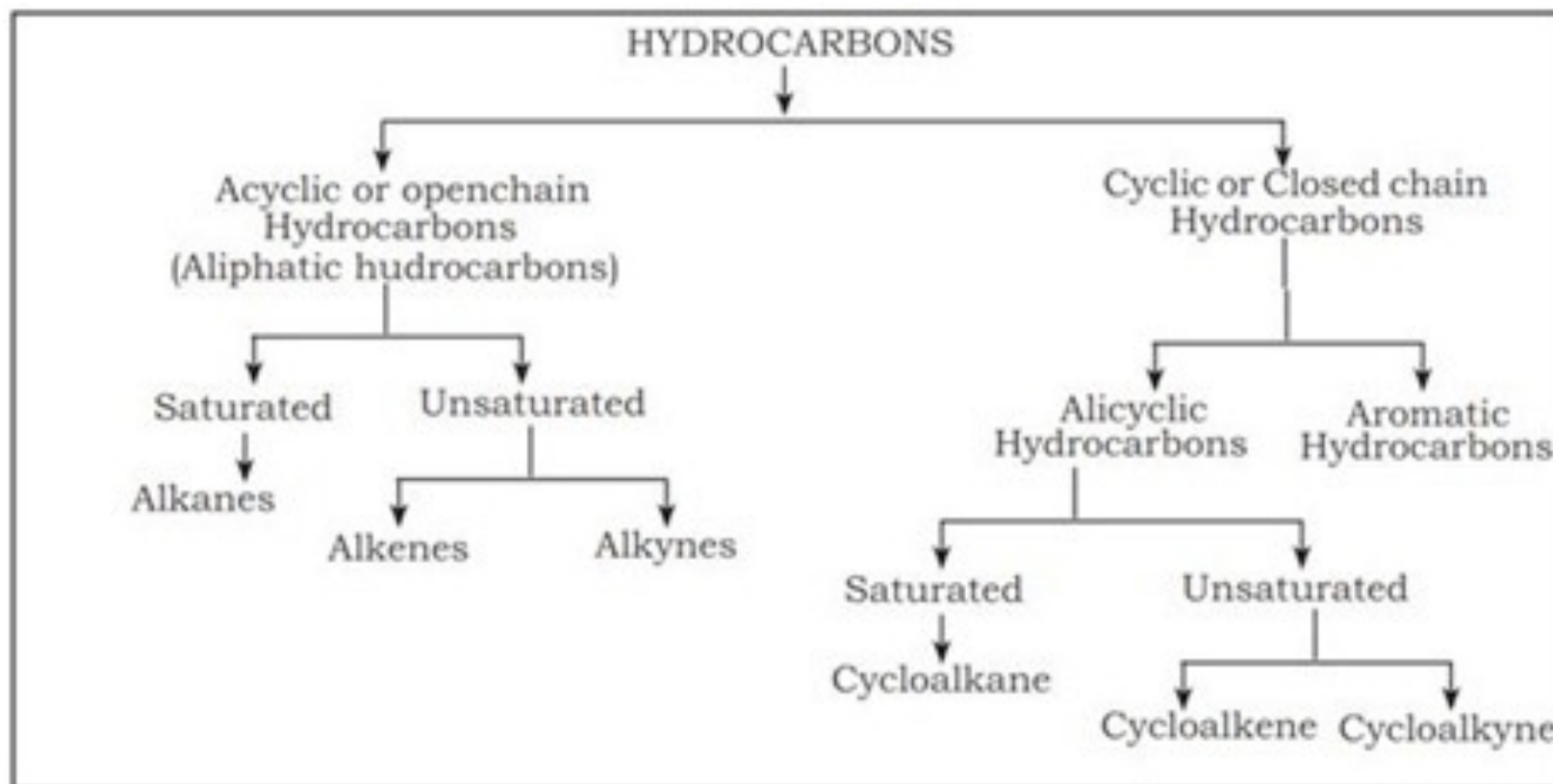
Hydrocarbons

- 1 **Aliphatic** open chain
- 2 **Cyclic** contain rings
- 3 **Aromatic** containing at least one benzene ring
- 4 **Heterocyclic** rings with one or more atom different from carbon.



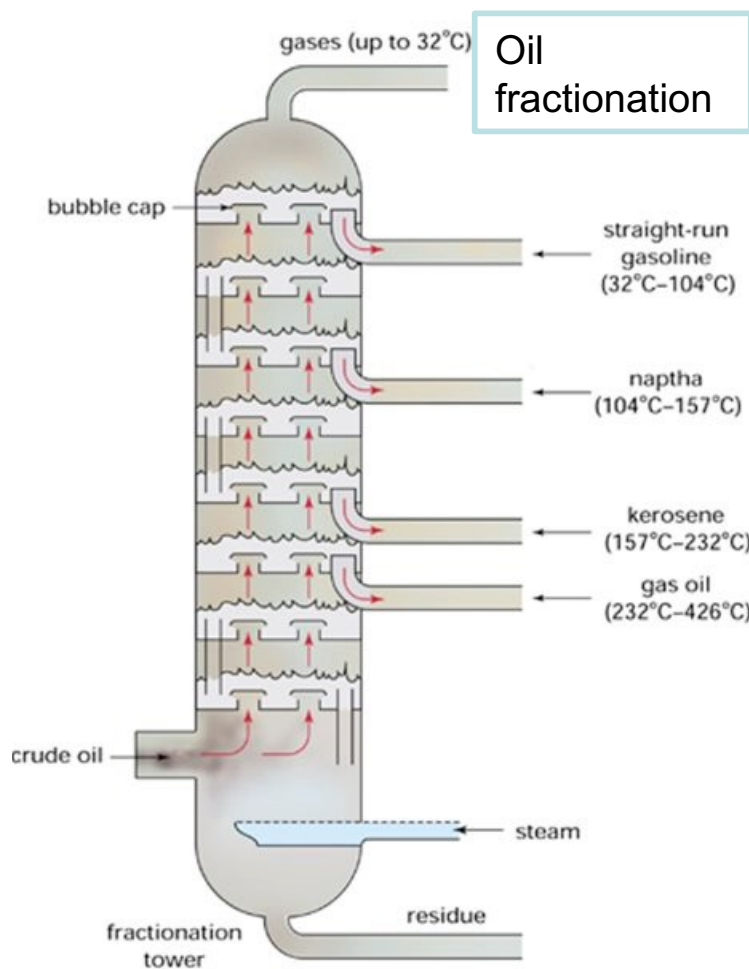
Hydrocarbon Classification

Compounds of carbon and hydrogen.



Hydrocarbons

They are the basic molecules of organic chemistry since, in addition to being very numerous, all other compounds can be considered as derivatives by replacing a hydrogen atom with a so-called functional group, i.e. chemical group, conferring to the compound characteristics different from those of the hydrocarbon of origin.



Hydrocarbon name	Chemical formula	Petroleum products
Methane	CH_4	Natural gas
Ethane	C_2H_6	
Propane	C_3H_8	LPG
Butane	C_4H_{10}	
Pentane	C_5H_{12}	Gasoline
Hexane	C_6H_{14}	
Heptane	C_7H_{16}	
Octane	C_8H_{18}	
Nonane	C_9H_{20}	Kerosene
Decane	$C_{10}H_{22}$	
Undecane	$C_{11}H_{24}$	
Dodecane	$C_{12}H_{26}$	Diesel fuel
Tridecane	$C_{13}H_{28}$	
Tetradecane	$C_{14}H_{30}$	Petrolatum
Pentadecane	$C_{15}H_{32}$	
Hexadecane	$C_{16}H_{34}$	
Heptadecane	$C_{17}H_{36}$	
Octadecane	$C_{18}H_{38}$	Petrolatum
Nonadecane	$C_{19}H_{40}$	
Eicosane	$C_{20}H_{42}$	

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Alkanes physical properties

Alkanes are *apolar* and involve only covalent, symmetric bonds.

✓ *Solubility?*  *Water insoluble.*

Intermolecular interactions are due to weak Van der Waals forces, that become relevant in large molecules, since they sum up depending on the size .

Physical Properties of Alkanes, $\text{CH}_3(\text{CH}_2)_{n-1}\text{H}$

n	Name	Bp, °C (760 mm)	Mp, °C	Density at 20°, d_4^{20} , g ml ⁻¹
1	methane	-161.5	-183	0.424 ^a
2	ethane	-88.6	-172	0.546 ^a
3	propane	-42.1	-188	0.501 ^b
4	butane	-0.5	-135	0.579 ^b
5	pentane	36.1	-130	0.626
6	hexane	68.7	-95	0.659
7	heptane	98.4	-91	0.684
8	octane	125.7	-57	0.703
9	nonane	150.8	-54	0.718
10	decane	174.1	-30	0.730
11	undecane	195.9	-26	0.740
12	dodecane	216.3	-10	0.749
15	pentadecane	270.6	10	0.769
20	eicosane	342.7	37	0.786 ^c
30	triacontane	446.4	66	0.810 ^c

^aAt the boiling point. ^bUnder pressure. ^cFor the supercooled liquid.

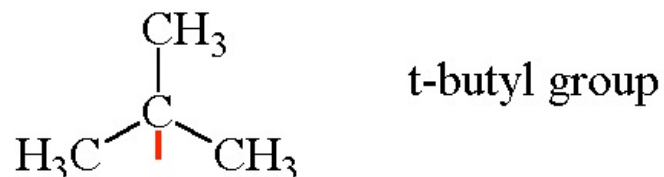
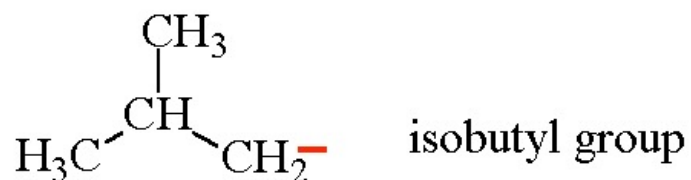
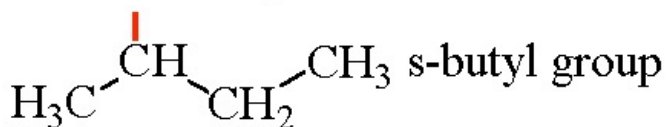
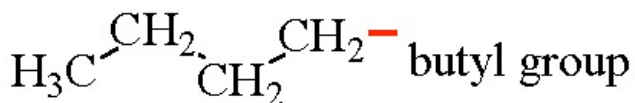
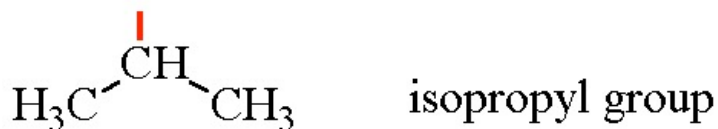
IUPAC Alkanes nomenclature

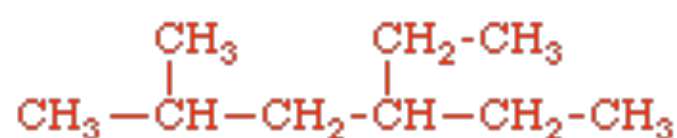
1. Choose the longest chain.
2. Consider the compound as a derivative, with H atoms substituted by alkyl groups. [alkyl groups: groups with a H less than the corresponding alkane. CH_3- , methyl; $\text{CH}_3\text{-CH}_2-$, ethyl; $\text{CH}_3\text{-CH}_2\text{-CH}_2-$, propyl; ec.]
3. Number the main chain atom in order to use the smallest number to indicate the substituent position.
4. If the same group appears more than once use the prefix *di-*, *tri-*, *tetra-*, etc.
5. If there are different groups, name them in alphabetic order.

No. of C atoms	Name of alkane	Molecular formula	Name of alkyl group	Formula
1	Methane	CH ₄	Methyl	-CH ₃
2	Ethane	C ₂ H ₆	Ethyl	-C ₂ H ₅
3	Propane	C ₃ H ₈	Propyl	-C ₃ H ₇
4	Butane	C ₄ H ₁₀	Butyl	-C ₄ H ₉
5	Pentane	C ₅ H ₁₂	Pentyl	-C ₅ H ₁₁
6	Hexane	C ₆ H ₁₄	Hexyl	-C ₆ H ₁₃
7	Heptane	C ₇ H ₁₆	Heptyl	-C ₇ H ₁₅
8	Octane	C ₈ H ₁₈	Octyl	-C ₈ H ₁₇
9	Nonane	C ₉ H ₂₀	Nonyl	-C ₉ H ₁₉
10	Decane	C ₁₀ H ₂₂	Decyl	-C ₁₀ H ₂₁

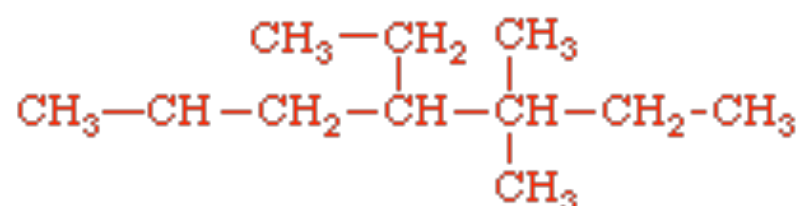
Names of alkyl groups

ALKYL GROUPS (8 common ones)

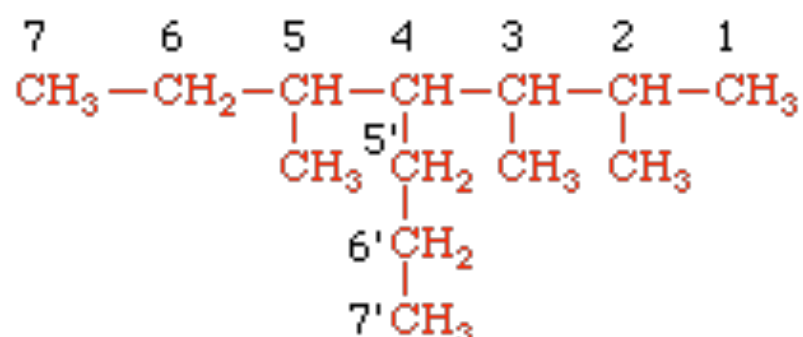




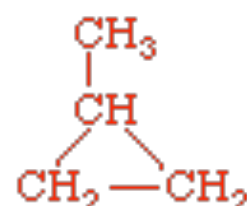
4-ethyl-2-methylhexane



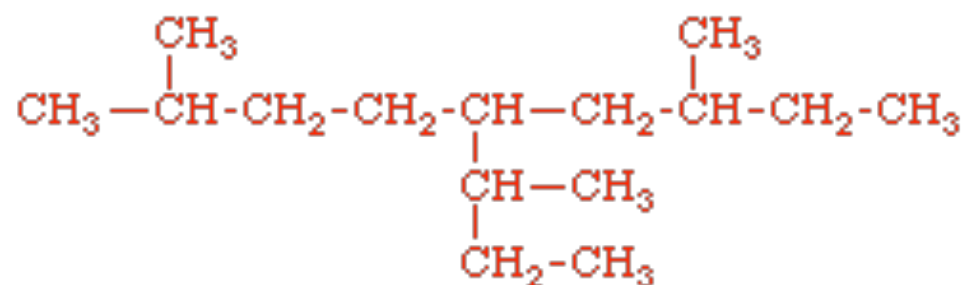
4-ethyl-3,3-dimethylheptane



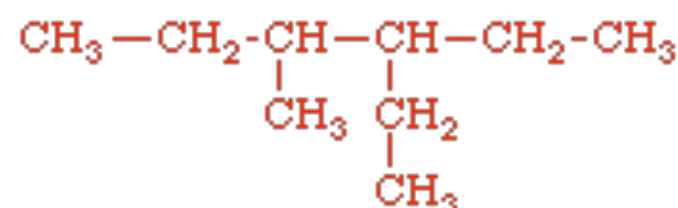
2,3,5-trimethyl-4-propylheptane
(NOT: 2,3-dimethyl-4-sec-butylheptane)



methylcyclopropane



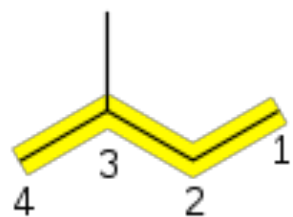
5-sec-butyl-2,7-dimethylnonane



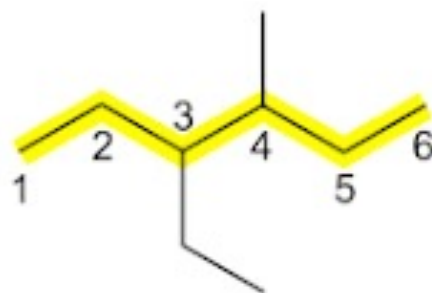
3-ethyl-4-methylhexane



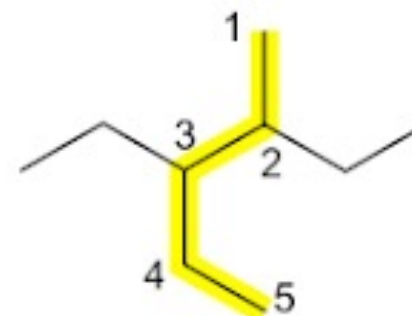
2-methylbutane
(correct numbering)



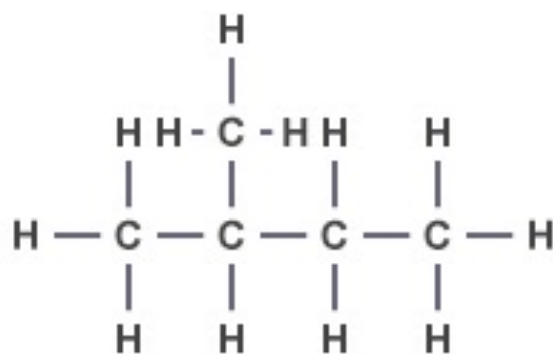
3-methylbutane
(incorrect numbering)



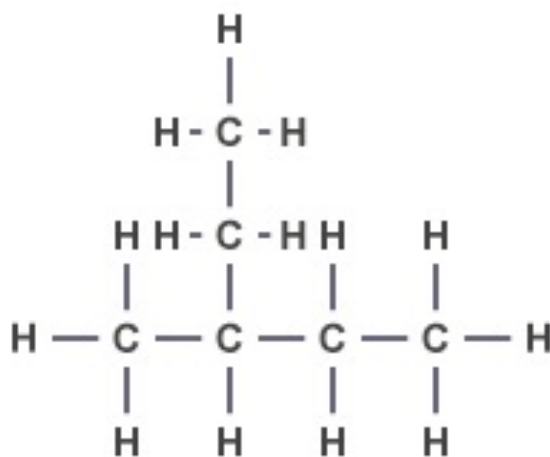
3-ethyl-4-methylhexane



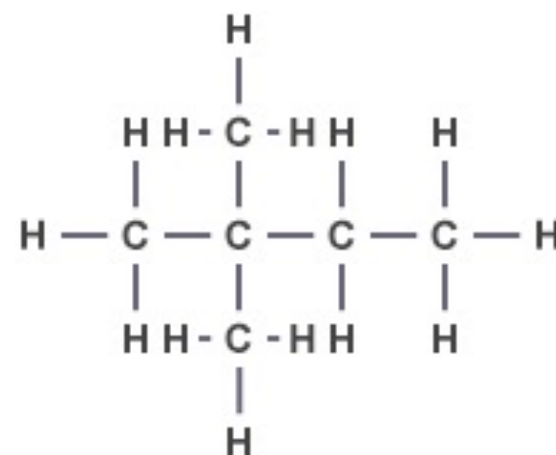
2,3-diethylpentane
(incorrect)



2-methylbutane



3-methylpentane
(not 2-ethylbutane)



2,2-dimethylbutane

Carbon atom classification

A carbon atom can be: **primary**, **secondary**, **tertiary** or **quaternary**, according to the number of carbon atoms to which it is bound.

$\begin{array}{c} \text{H} \ \text{H} \\ \ \ \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \ \ \\ \text{H} \ \text{H} \end{array}$	<p>Each C is attached to <u>one</u> other C atom; therefore, each is a <u>primary</u> C.</p>
$\begin{array}{c} \text{H} \ \text{H} \ \text{H} \\ \ \ \ \ \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \ \ \ \ \\ \text{H} \ \text{H} \ \text{H} \end{array}$	<p>The middle C (C#2) is attached to <u>two</u> other C atoms; therefore, it is a <u>secondary</u> C. (The end C's -- #1 & #3 -- are primary.)</p>
$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	<p>The top middle C is attached to <u>three</u> other C atoms; therefore, it is a <u>tertiary</u> C. (The three end C's are all primary.)</p> <p>Note that I used a condensed formula here. It doesn't matter. It is up to you to count the C atoms.</p>
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	<p>The middle C is attached to <u>four</u> other C atoms; therefore, it is a <u>quaternary</u> C. (The four end C's are all primary.)</p>

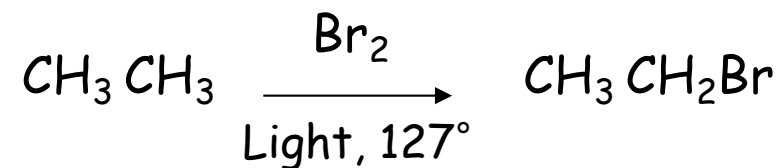
Methyl-propane

Dimethyl-propane

Alkanes reactions

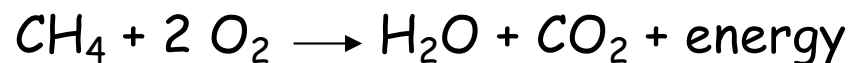
Alkanes are inert toward most reagents and they react in drastic conditions

Alogenation



Oxidation

Alkanes are not easily oxidized, and when they do they achieve the most oxidized state (CO_2):



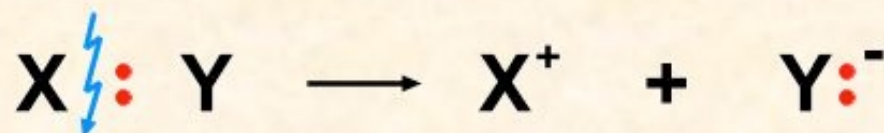
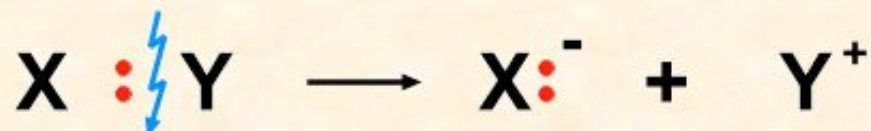
BREAKING COVALENT BONDS

There are **3 ways to split** the shared electron pair in an **unsymmetrical** covalent bond.

UNEQUAL SPLITTING

produces **IONS**

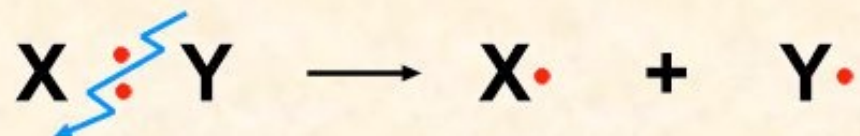
known as **HETEROLYSIS** or
HETEROLYTIC FISSION



EQUAL SPLITTING

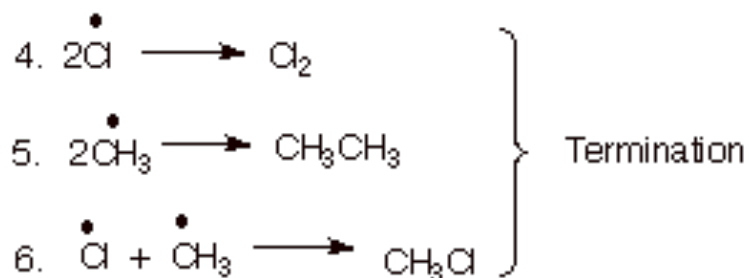
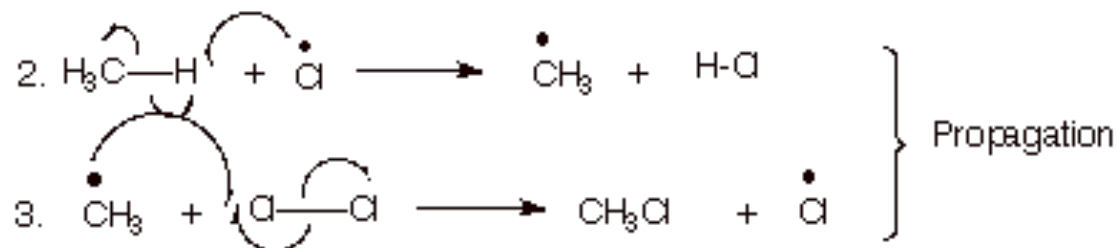
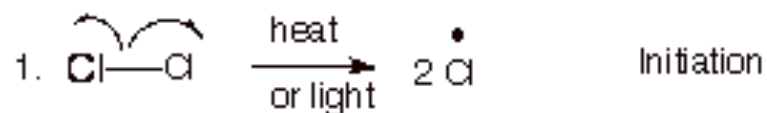
produces **RADICALS**

known as **HOMOLYSIS** or
HOMOLYTIC FISSION

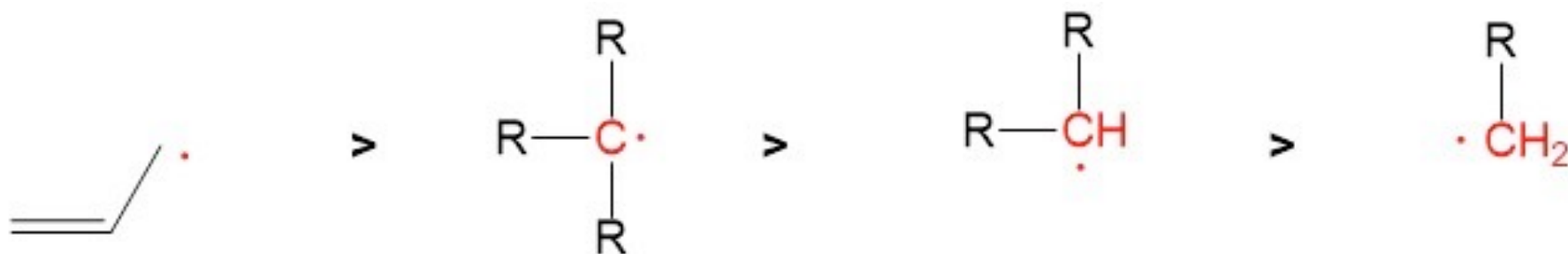


- If several bonds are present the **weakest bond is usually broken first**
- Energy to break bonds can come from a variety of energy sources - heat / light
- In the reaction between methane and chlorine either can be used, however...
- In the laboratory a source of UV light (or sunlight) is favoured.

Mechanism of radicalic halogenation (substitution)



Alkane radicals stability

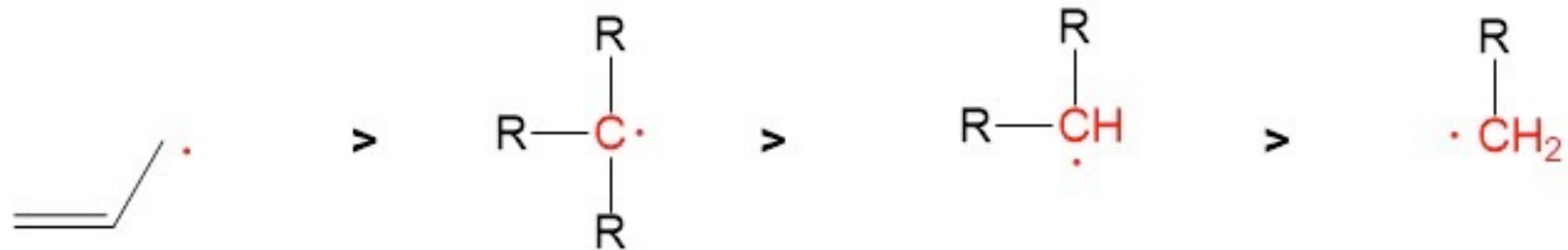


Carbon adjacent to alkene
allylic position

3 "R" substituents
tertiary center (3°)

2 "R" substituents
secondary center (2°)

1 "R" substituent
primary center (1°)



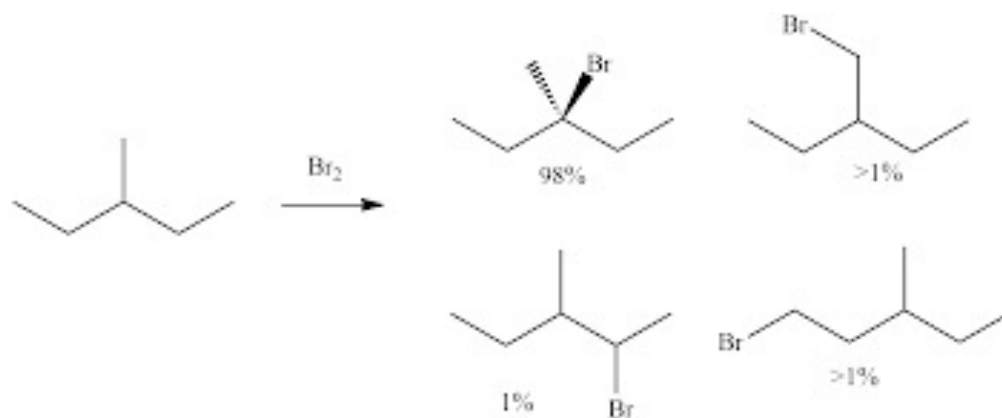
Carbon adjacent to alkene
allylic position

3 "R" substituents
tertiary center (3°)

2 "R" substituents
secondary center (2°)

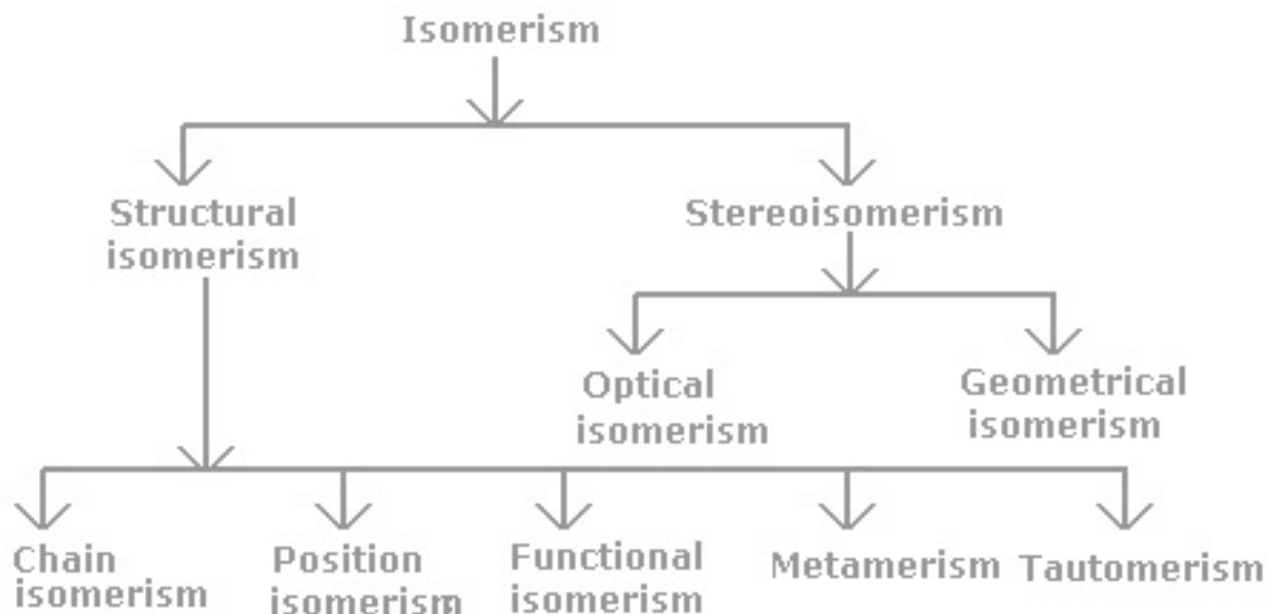
1 "R" substituent
primary center (1°)

The product halogenated on tertiary C is more abundant, due to the relative stability of the radicals



ISOMERISM

Isomerism indicates the fact that substances that have the same formula and **molecular mass**, differ for physical properties and often also for chemical behaviour due to differences in the structure.



Isomerism

Do the compounds have the same molecular formulae?

NO

Not isomers

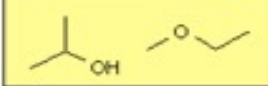
YES

Isomers

Do the compounds have the same connectivity?

NO

Constitutional



YES

Stereoisomers

Can the compounds be interconverted by rotation about single bonds?

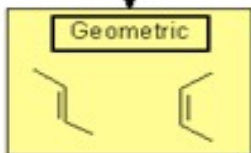
NO

Configurational

Is the isomerism at a double bond?

YES

Geometric



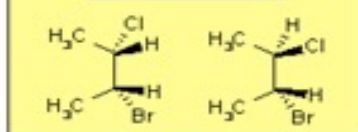
NO

Optical

Are the compounds non-superimposable mirror images?

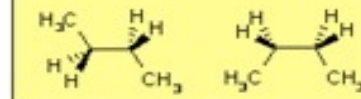
NO

Diastereomers



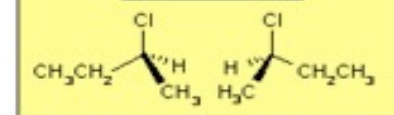
YES

Conformational



YES

Enantiomers



Structural isomerism

Chain isomerism

Position isomerism

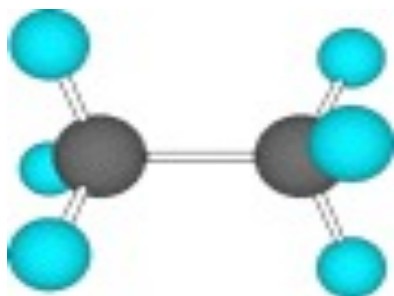
Functional isomerism

Metamerism

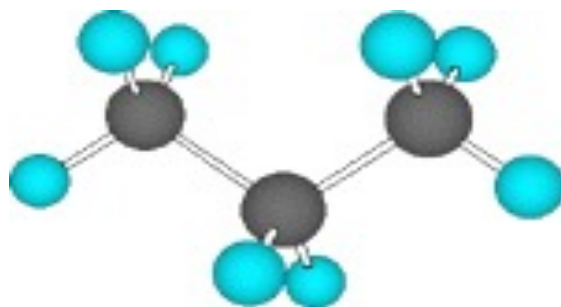
Tautomerism

Ring-chain isomerism

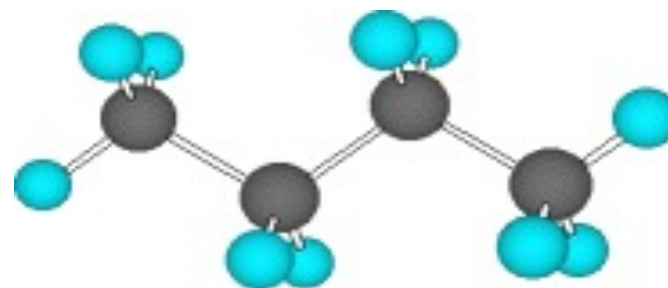
ALKANES



ethane (C_2H_6)



propane (C_3H_8)



butane (C_4H_{10}).

From butane on we find **isomerism**, when *two molecules hav same formula but different structure*.

Butane has two isomers: *normalbutane (n-butane)* and *isobutane (or methylpropane)*.

The larger the number of C atoms the larger the number of isomers:

C_4H_{10} -> 2 isomers

C_5H_{12} -> 3 isomers

C_6H_{14} -> 5 isomers

C_7H_{16} -> 9 isomers

C_8H_{18} -> 18 isomers

C_9H_{20} -> 35 isomers

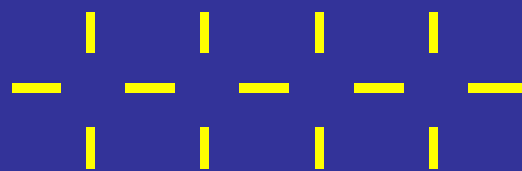
.....

$C_{40}H_{82}$ -> 62.491.178.805.831 isomers

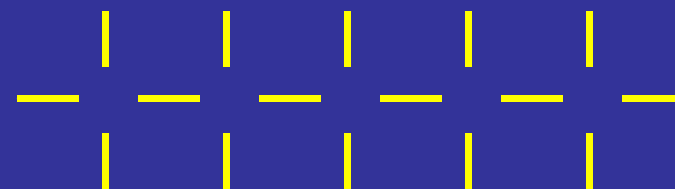
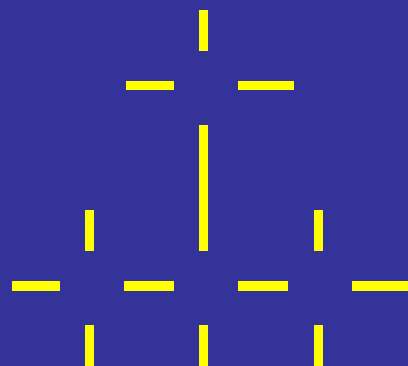
Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Isomerism of alkanes:

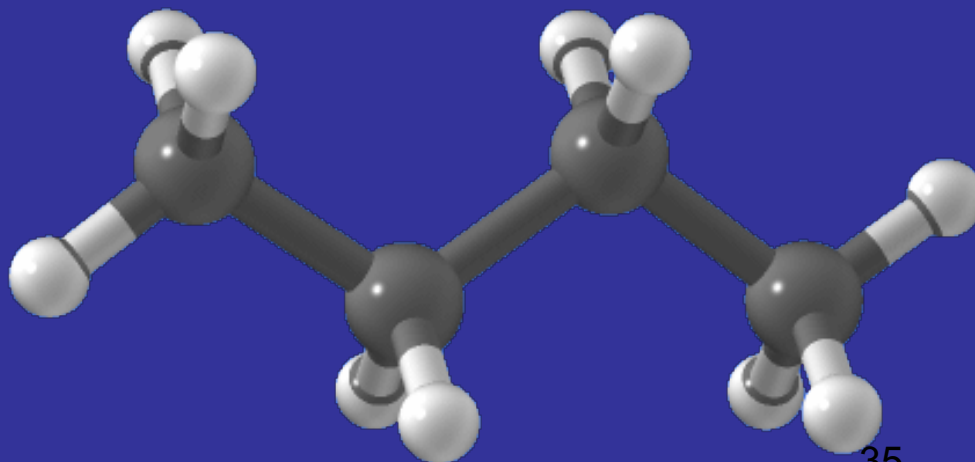
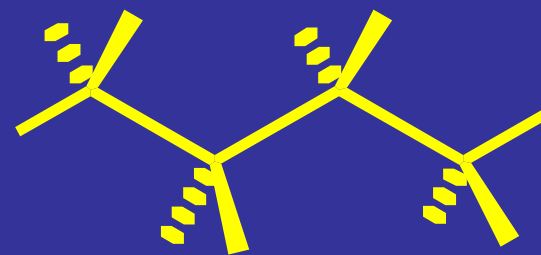
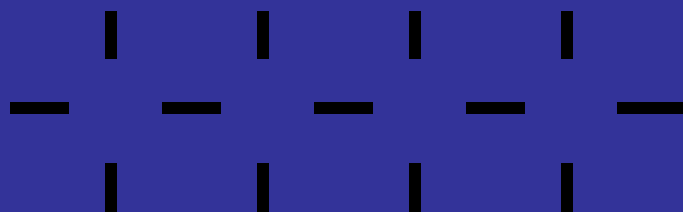
How many
 C_5H_{12} ?



butane (C_4H_{10})



Butane = C_4H_{10} , $CH_3CH_2CH_2CH_3$

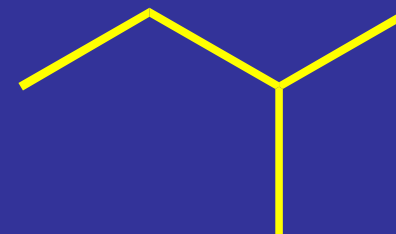


Simplified structure

How many isomers for C_5H_{12} ?

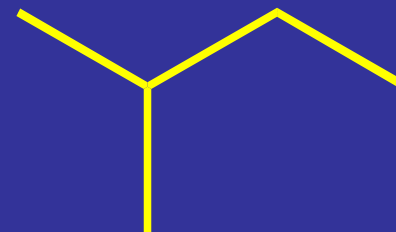


Identical structures

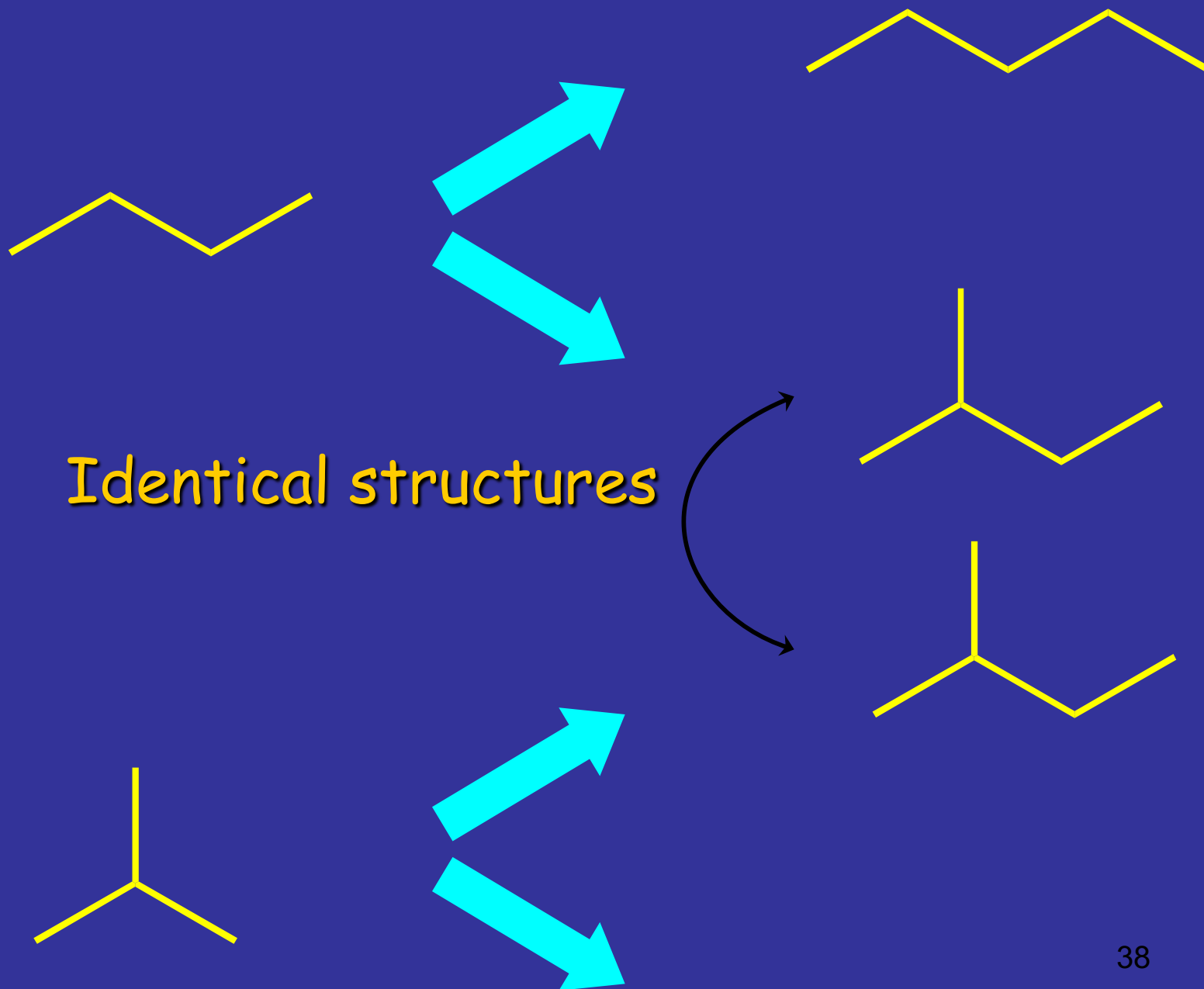




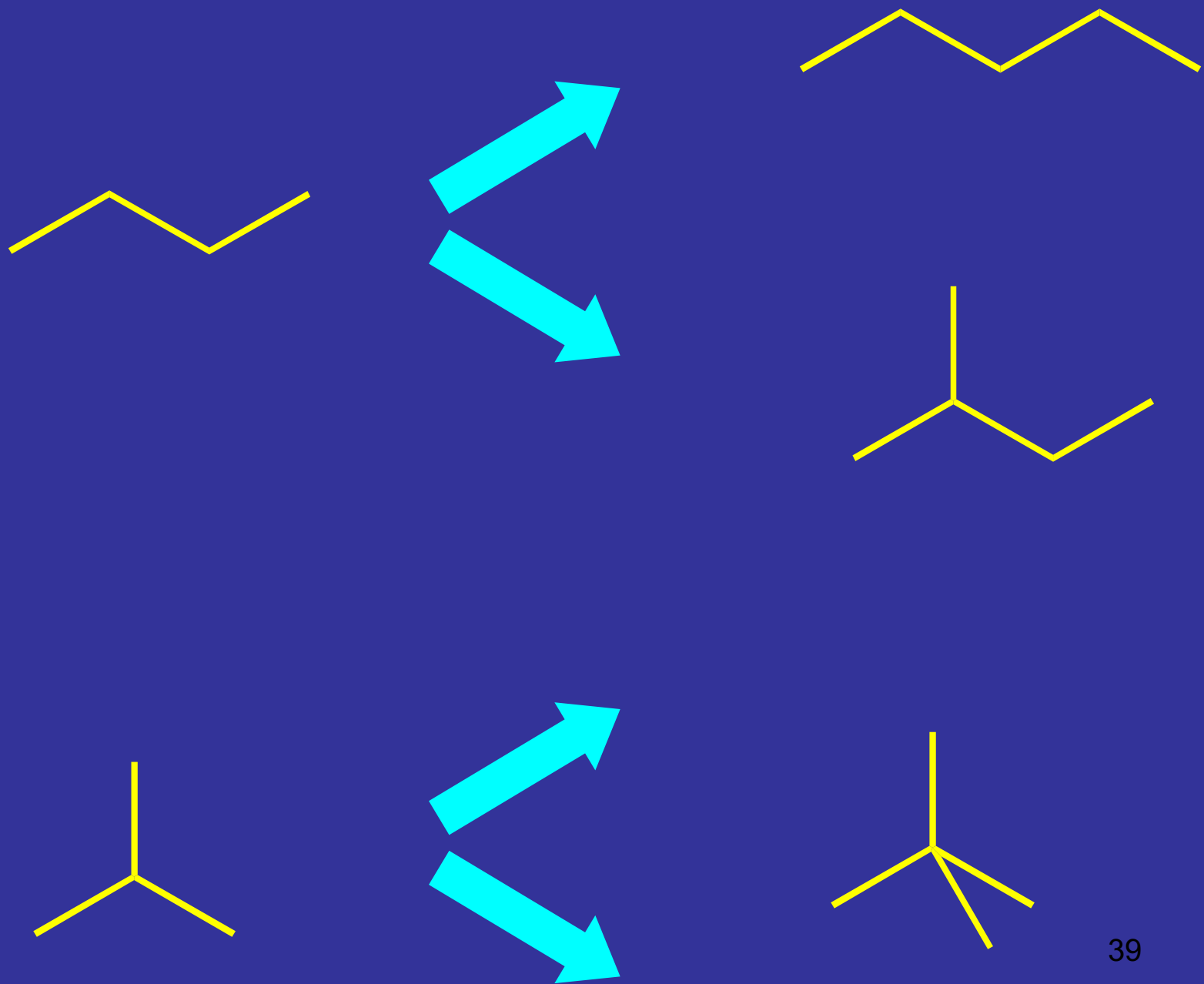
Identical structures



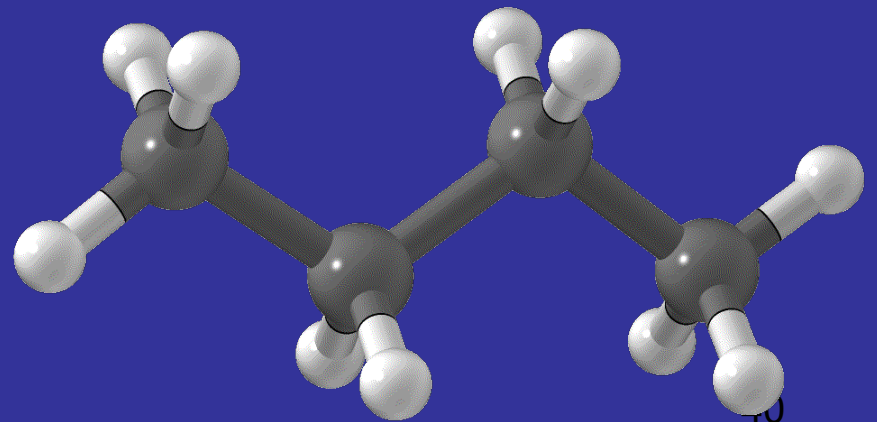
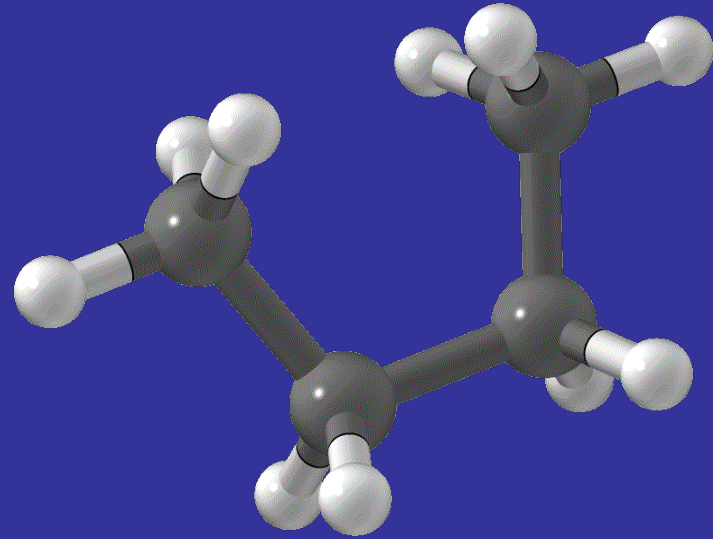
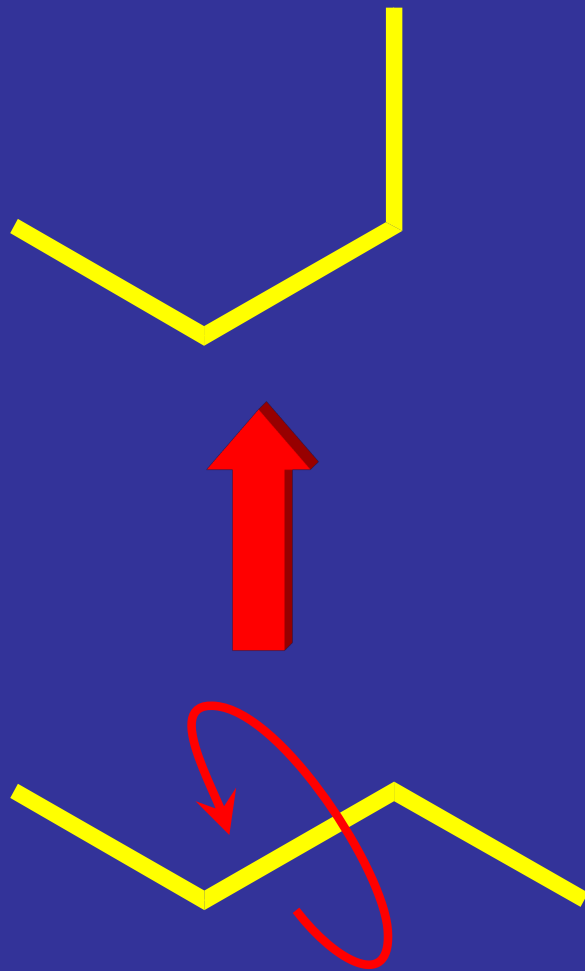
Isomers of alkanes: How many C_5H_{12} ?



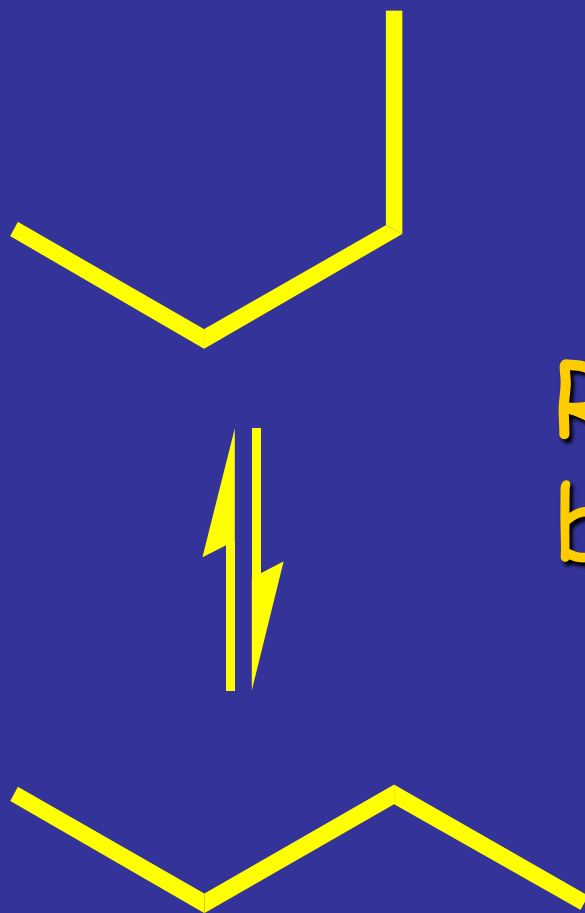
Isomers of alkanes: How many C_5H_{12} ?



Butane, bond rotation

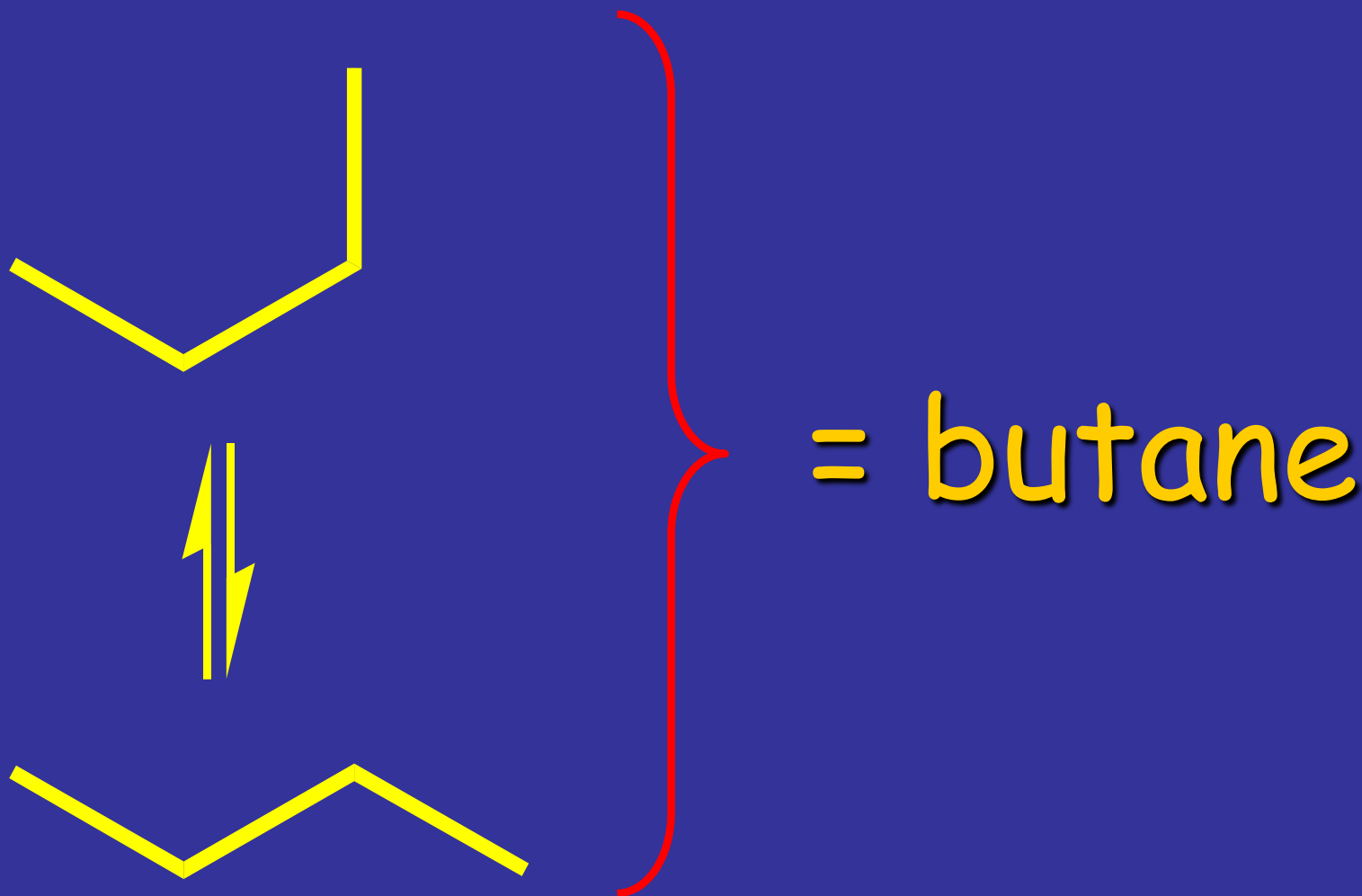


Butane, bond rotation

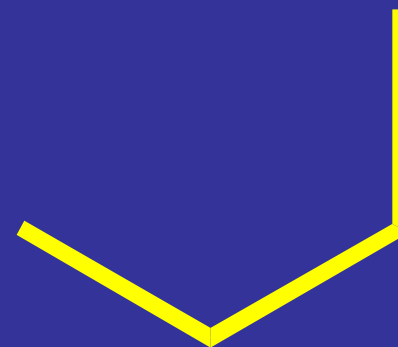


Rotation around single bonds is fast.

Butane, bond rotation



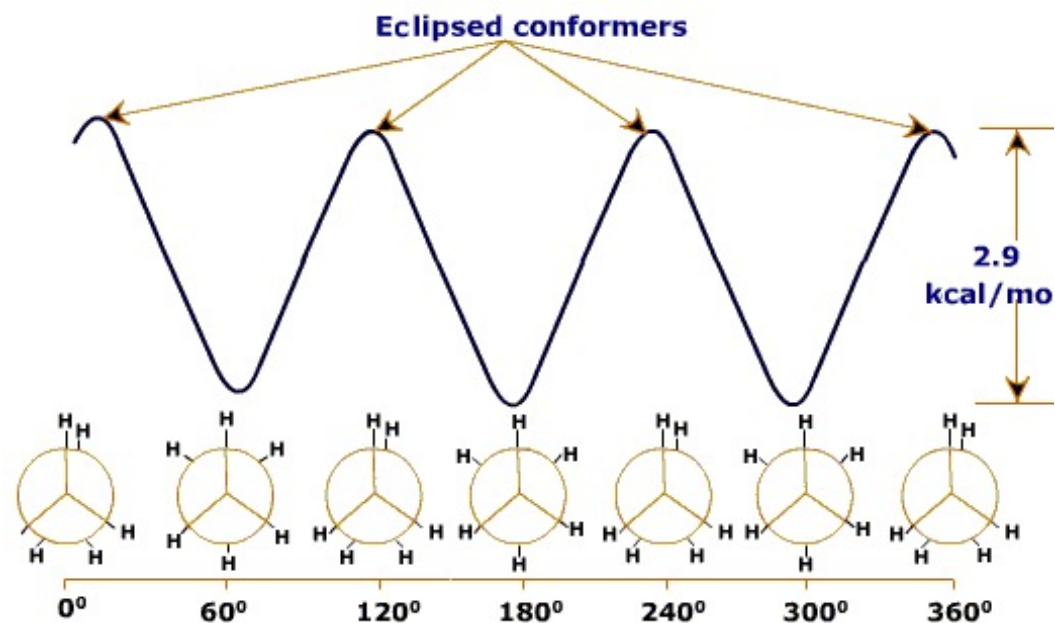
Isomers of C_4H_{10} .



Stereoisomerism

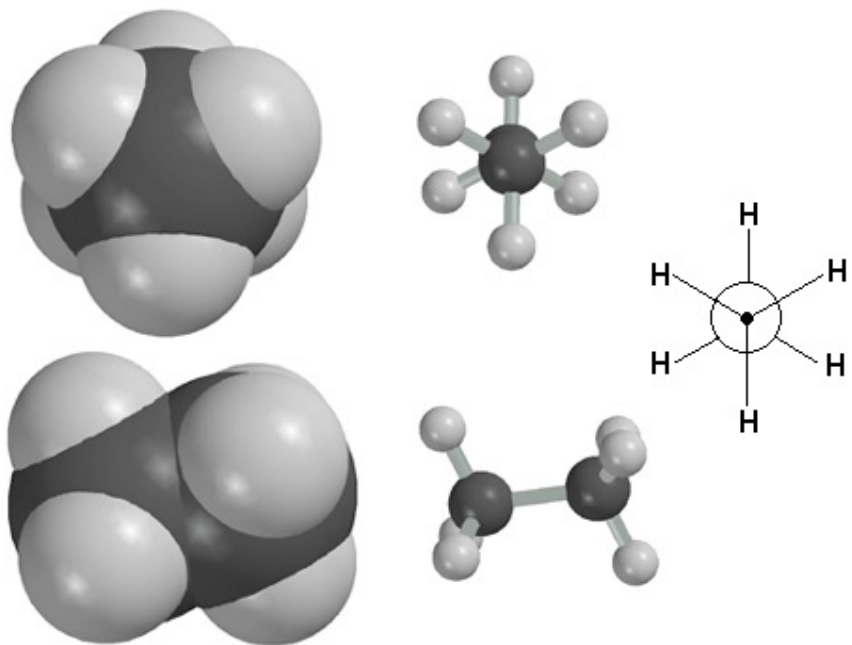
Conformational isomerism: the different structures are converted without breaking bonds. Interconversion, same compound.

The σ bond can rotate \rightarrow the structure of ethane can assume all conformations from eclipsed to staggered.

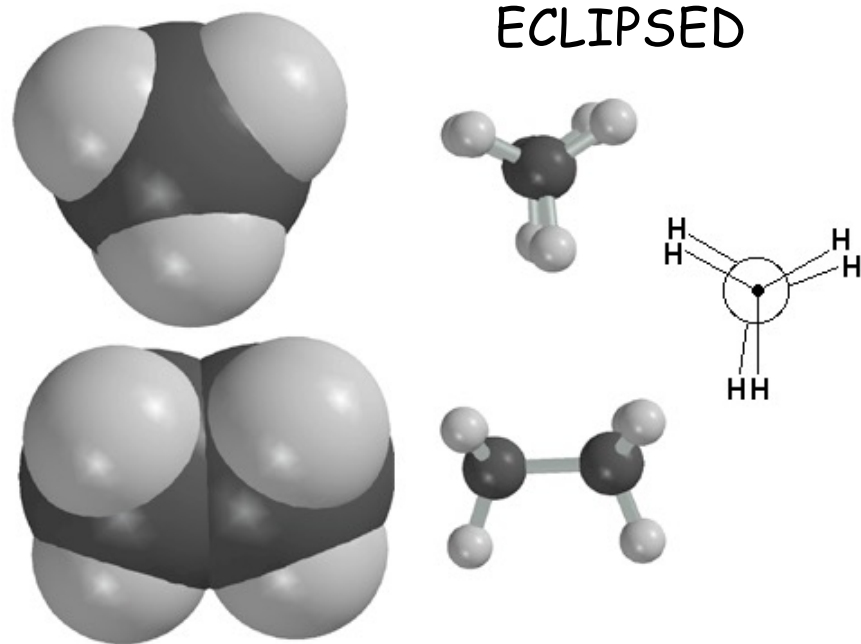


The staggered conformation is more stable by 2.9 kcal/mole

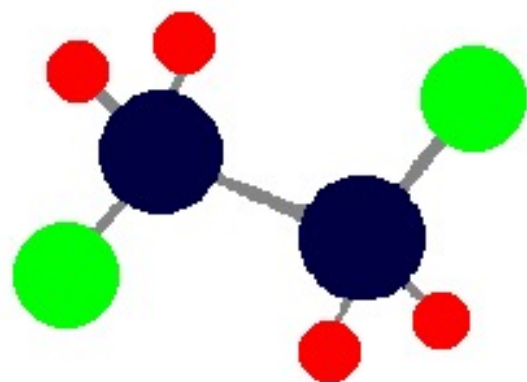
STAGGERED



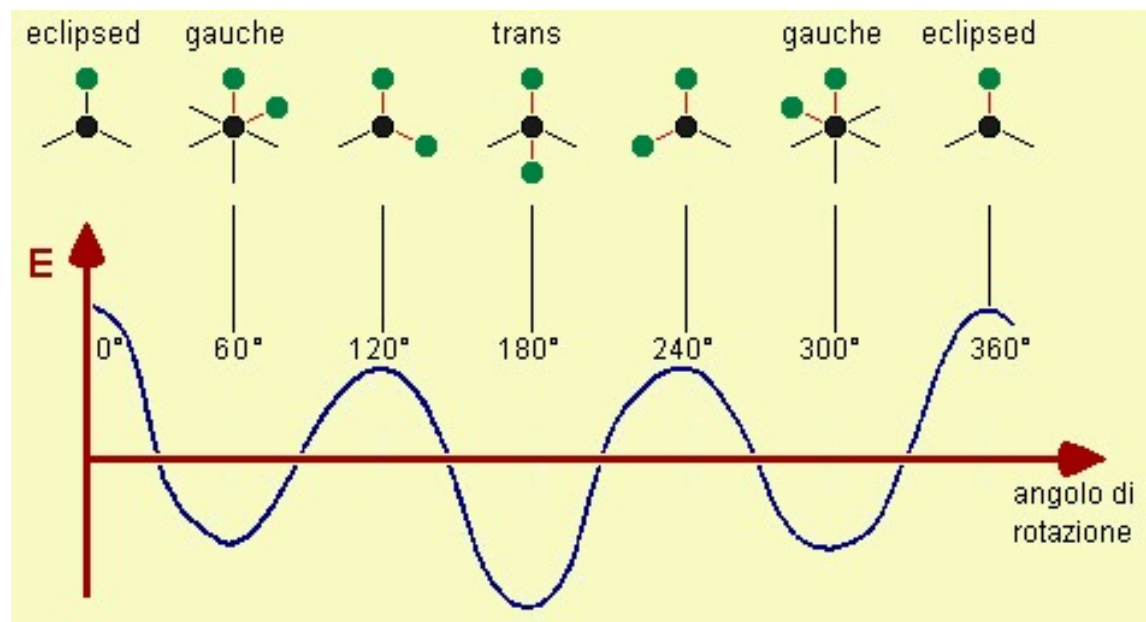
ECLIPSED



For molecules such as butane or 1,2 dichloroethane one finds relative and absolute minima.

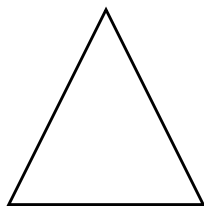


1,2-dichloroethane

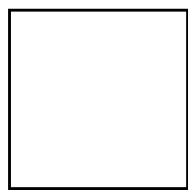


CICLOALKANES

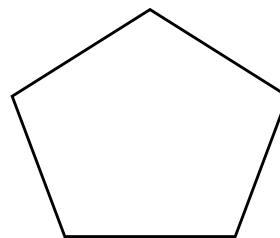
These are saturated hydrocarbons that have a closed chain.



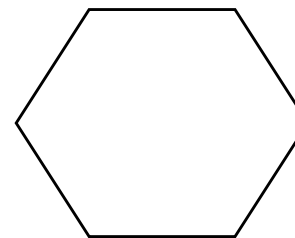
ciclopropane



ciclobutane



ciclopentane

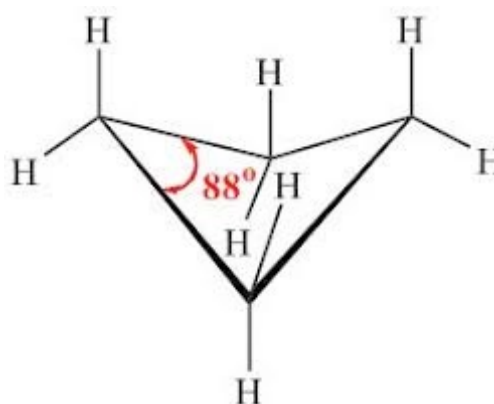


cyclohexane

They can have *addition reactions* that break the ring inducing the formation of linear alkanes.

This is due to the *ring tension* (angular tension) that destabilizes them.

- for a sp^3 carbon, the deviation from a tetrahedral geometry causes an **angular tension**.
- A couple of sp^3 carbons is more stable if their conformation is **staggered**.



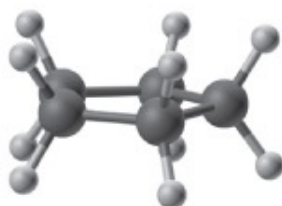
cyclobutane

cyclopentane

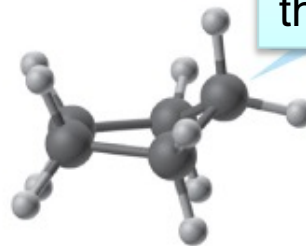
(a)



(b)



(c)



Folding partially relieves the angular tension

Planar conformation folded ("envelope") conformation

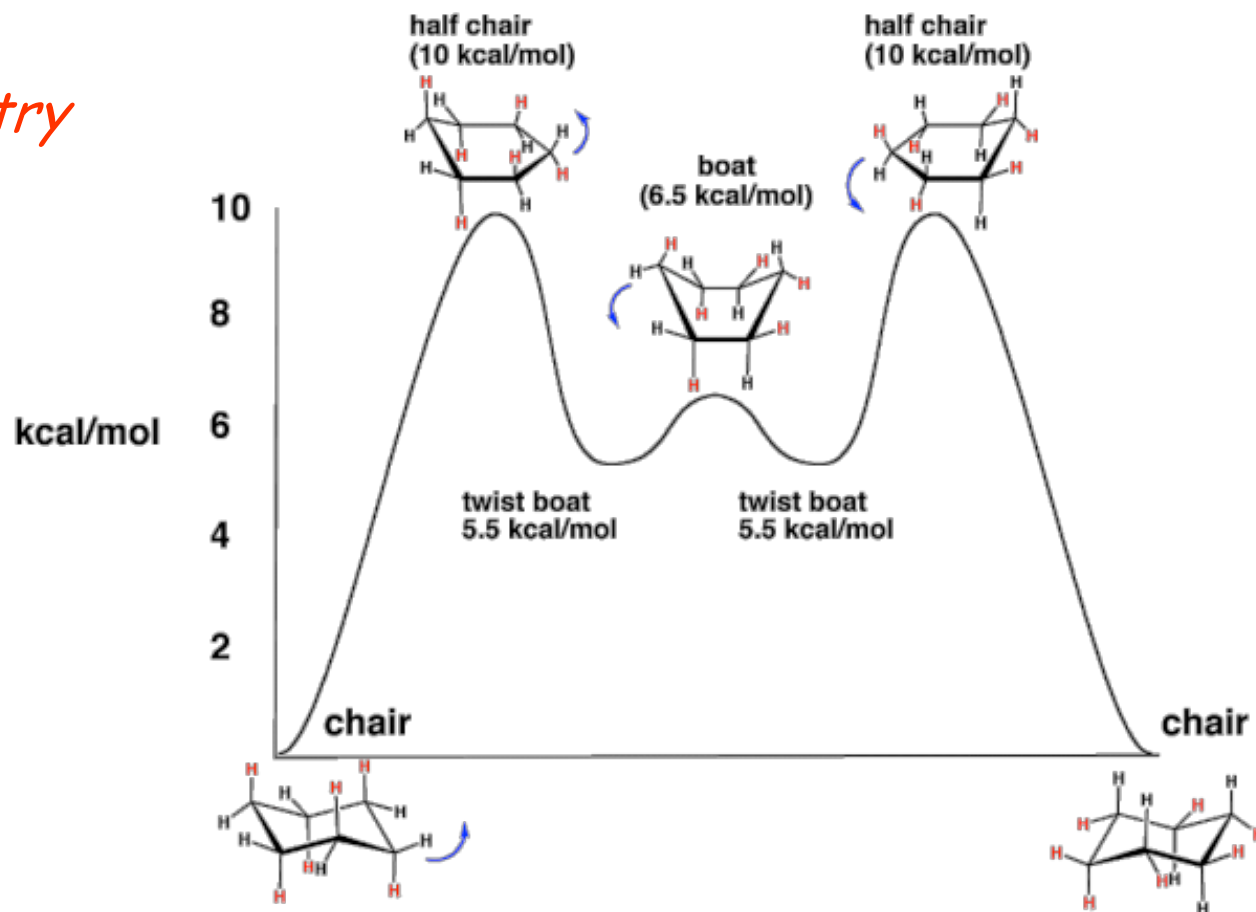
The "chair" conformation has no tension since

it has tetrahedral geometry and staggered conformation.

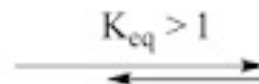
Axial and equatorial



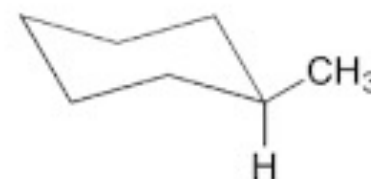
Cyclohexane Chair Flip Energy Diagram



methyl group axial



more stable by 7 kJ/mol

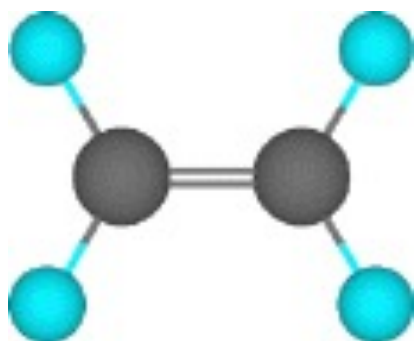


methyl group equatorial

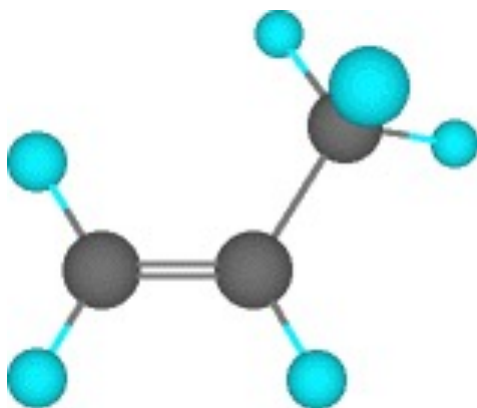
Insaturated hydrocarbons: **ALKENES**

Alkenes have at least a double π bond

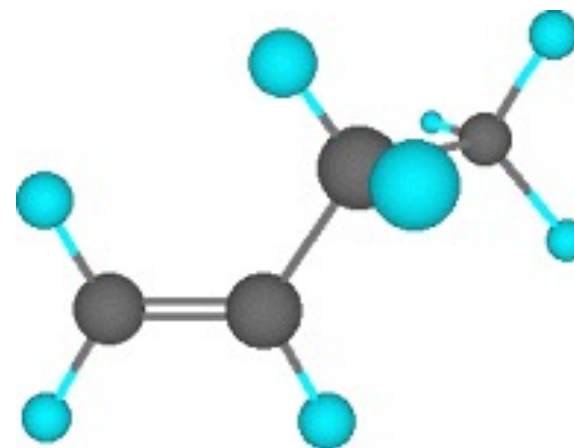
Their name has the suffix -ENE



Ethene
 C_2H_2



Propene
 (C_3H_6)

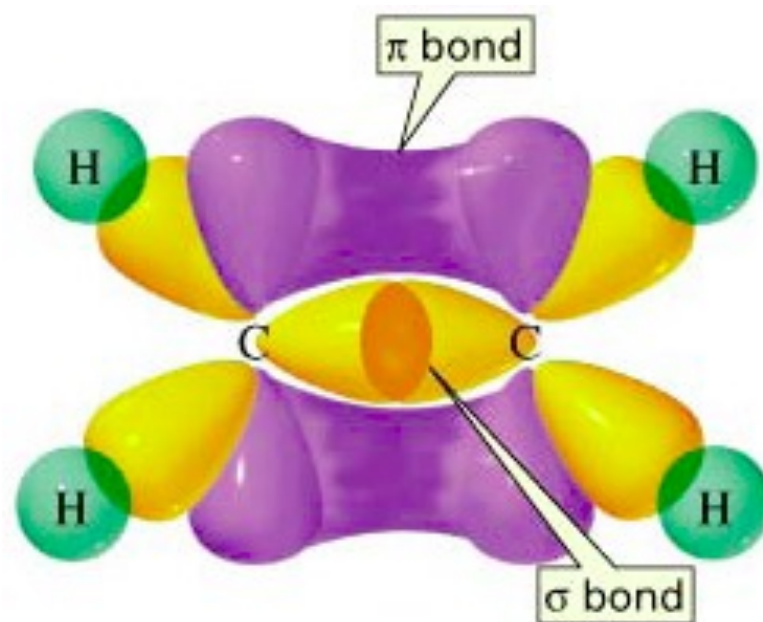
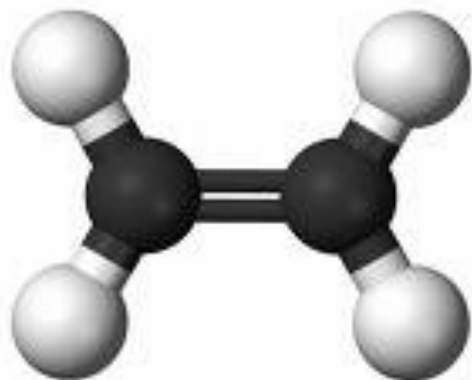


1-butene
 (C_4H_8) .

The **double-bond** involves a **σ bond** (83 kcal/mole), derived dalla from the overlap of **sp^2** orbital and a **π bond** (62 kcal/mole), from the partial overlap of **p** orbitals.

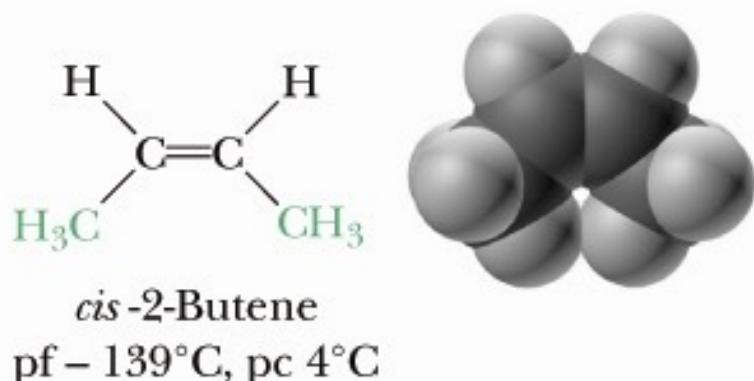
The double bond is **stronger** than a single one (145 vs 83 kcal/mole) and **shorter** (1,34 vs 1,53 Å).

The molecule is planar

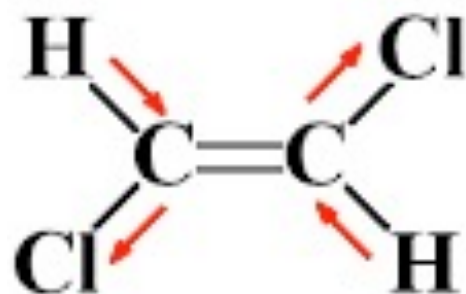
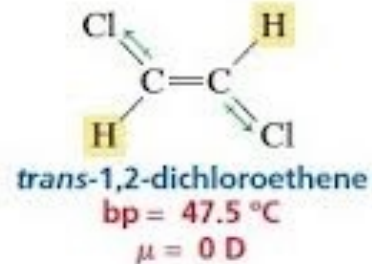
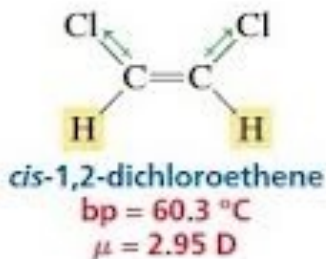
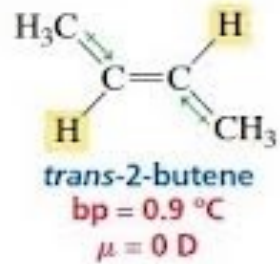
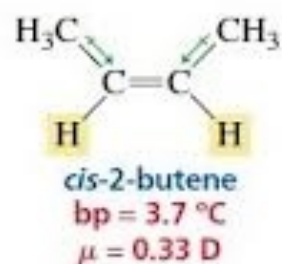


Geometric isomerism

Depending on the position of the bond we can have 1-butene or 2-butene; 2-butene can have two structures:



These are **stereoisomers**. Their difference is in the spatial arrangement and not in the bond order. More precisely they are **diastereoisomers** since they are not mirror images.



trans-1,2-dichloroethene
 $\mu = 0$ D



cis-1,2-dichloroethene
 $\mu = 1.89$ D

Bond Moments cancel out in *trans*
but do not cancel out in *cis*.
The Dipole Moment is the
Vector Sum of all the Bond Moments

Isomerism

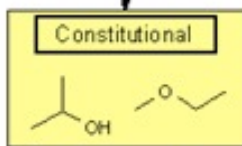
Do the compounds have the same molecular formulae?

NO
Not isomers

YES
Isomers

Do the compounds have the same connectivity?

NO



YES

Stereoisomers

Structural isomerism

Chain isomerism

Position isomerism

Functional isomerism

Metamerism

Tautomerism

Ring-chain isomerism

Can the compounds be interconverted by rotation about single bonds?

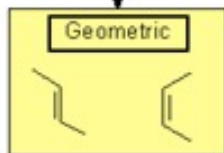
NO

Configurational

Is the isomerism at a double bond?

YES

Geometric



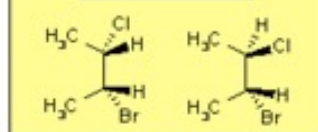
NO

Optical

Are the compounds non-superimposable mirror images?

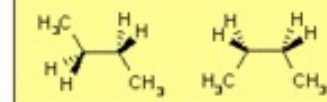
NO

Diastereomers



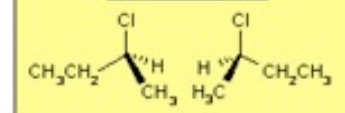
YES

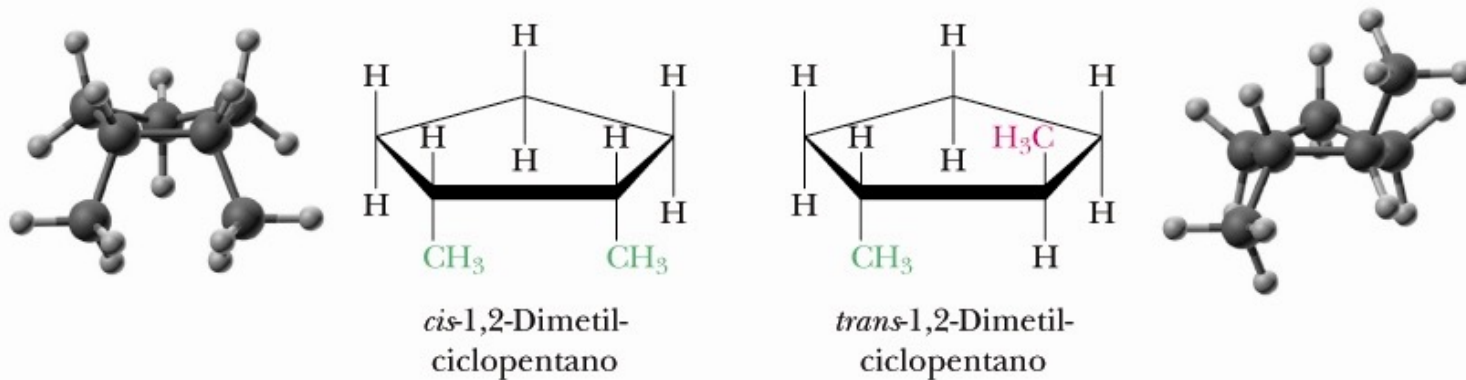
Conformational



YES

Enantiomers





Geometric isomerism (*cis-trans*) is present whenever a bond can not rotate, including cyclic compounds.

