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:

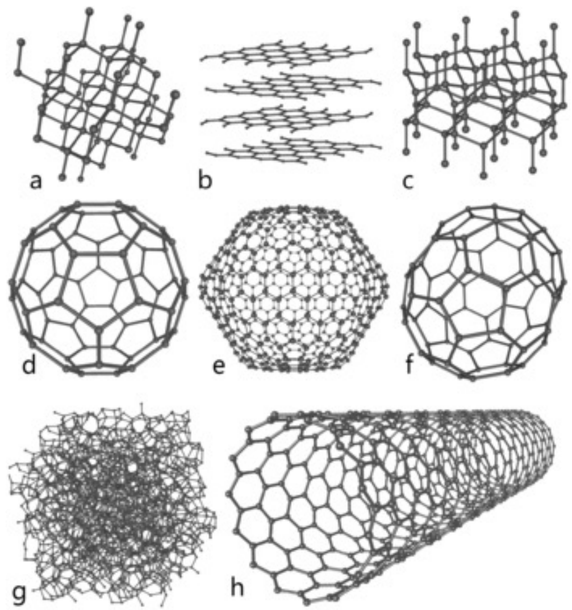
All organic compounds contain carbon.

- 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)

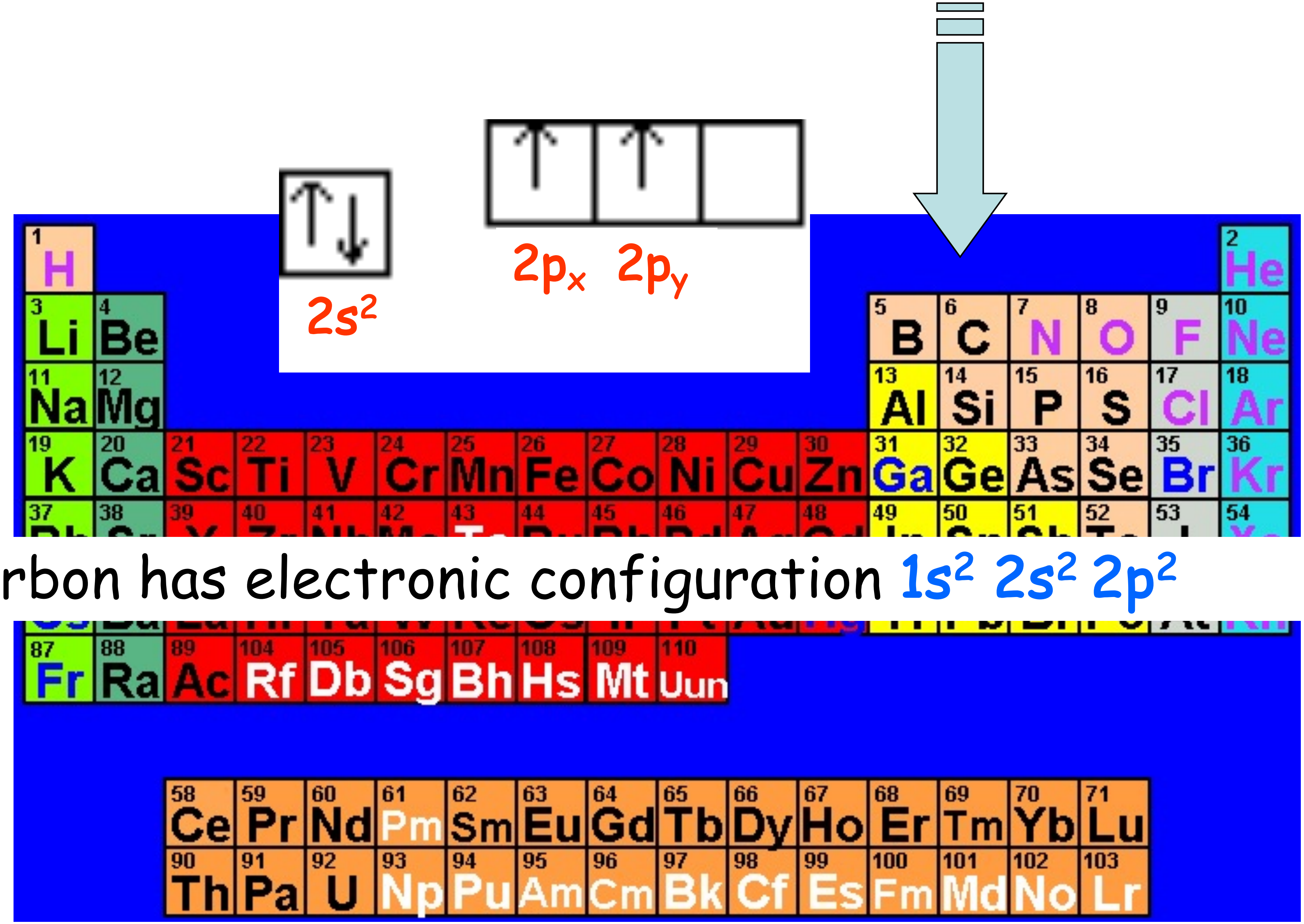
- The oxidation product of silicon SiO_2 is a solid, Whereas CO_2 is a gas.

- 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



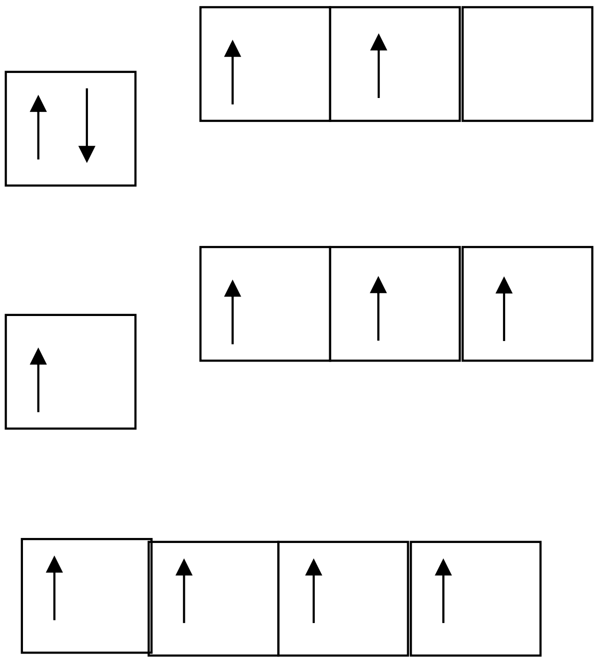
Carbon has electronic configuration $1s^2\ 2s^2\ 2p^2$

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

Ibridization: with a modest energy cost (compensated by the formation of *4 bonds 4 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: $1s^2\ 2s\ 2p^3$.

$1s^2\ 2s^2\ 2p^2$

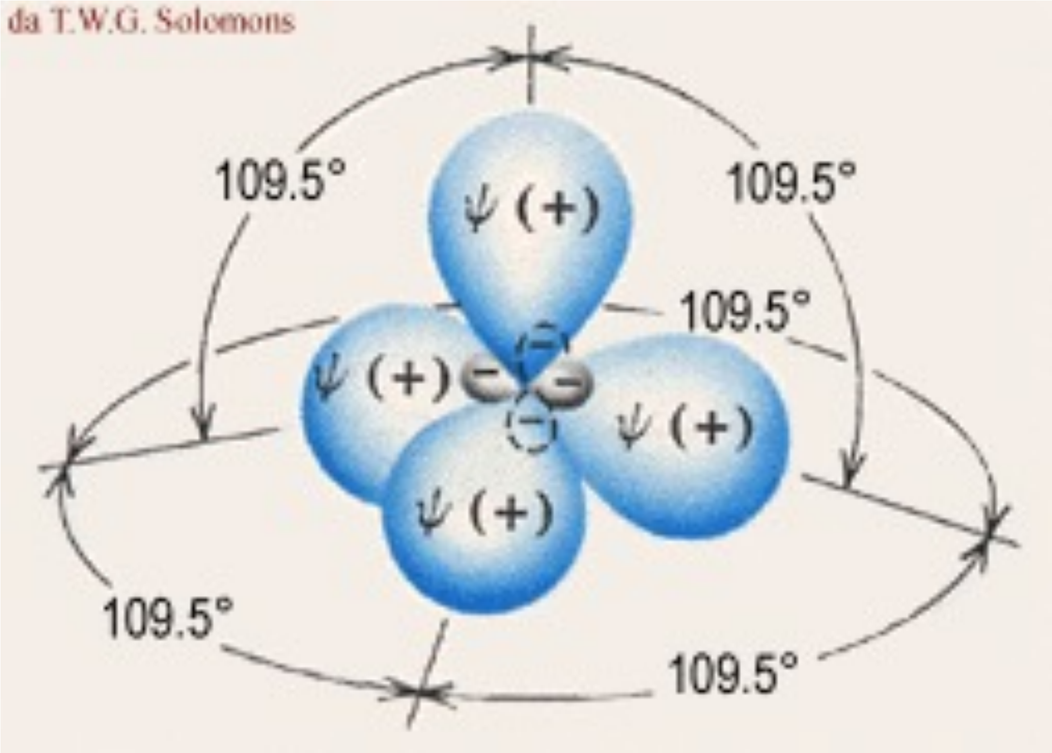
$1s^2\ 2s\ 2p^3$



Hybrid orbital sp^3

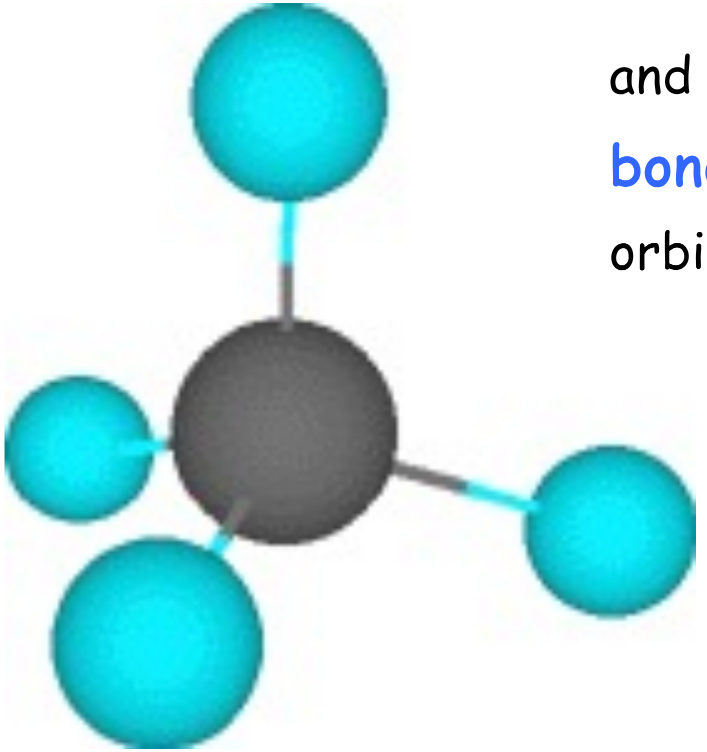
4 energetically equivalent orbitals

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 tethahedron (109° 28').

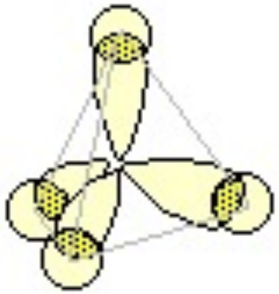


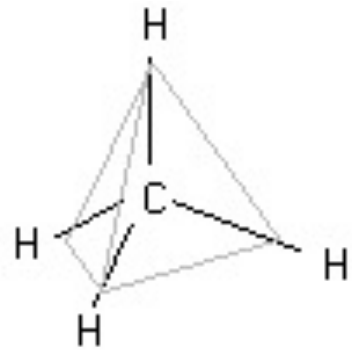
Ibridazione sp^3

Methane: CH_4



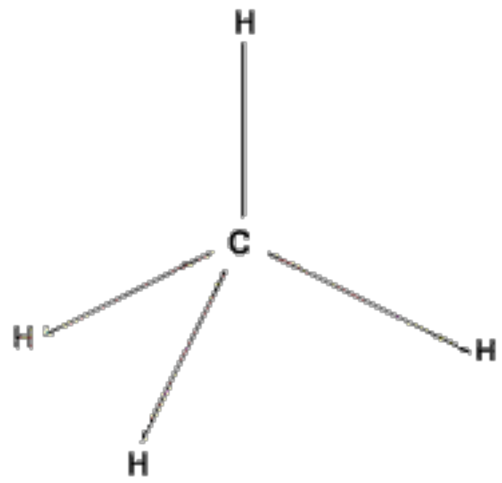
The bond arising from a carbon sp^3 electron and the hydrogen 1s electron is a σ bond(direction bond with maximum overlas of orbitals)



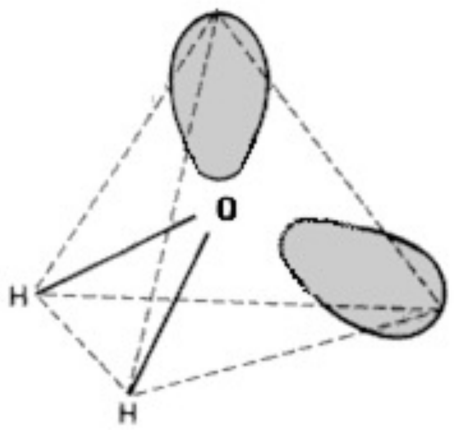


These are the bonds found in ALKANES where carbon forms 4 σ *bonds with a tetrahedral geometry..*

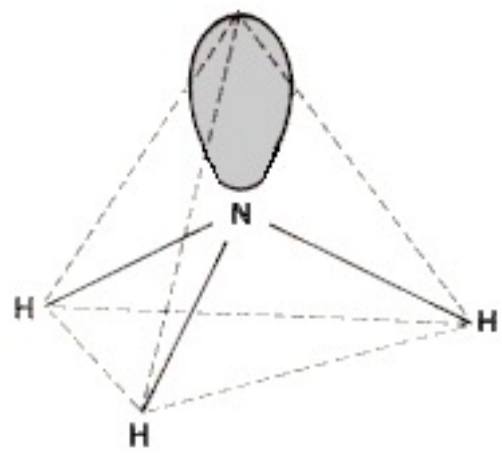
Tetrahedrical geometries compared: sp^3 hybridization



Methane: CH_4

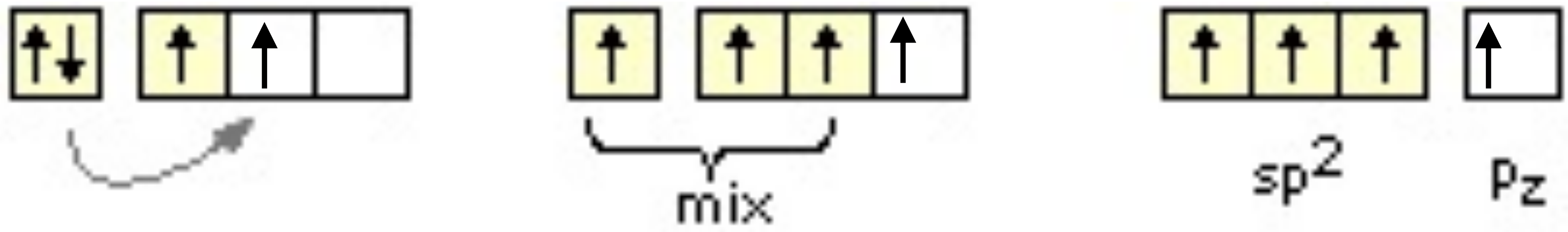


Water H_2O



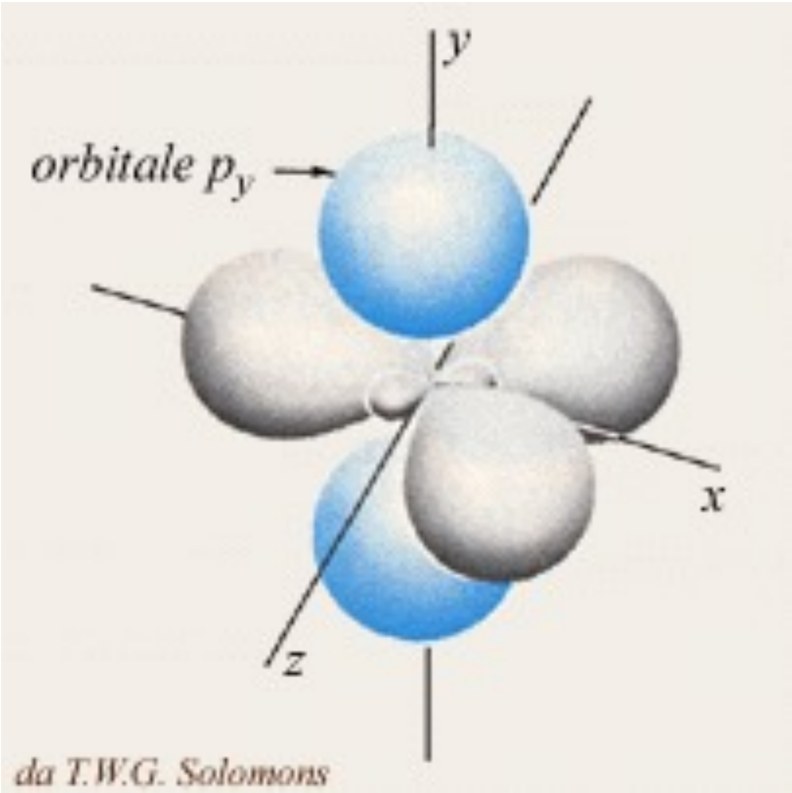
Ammonia NH_3

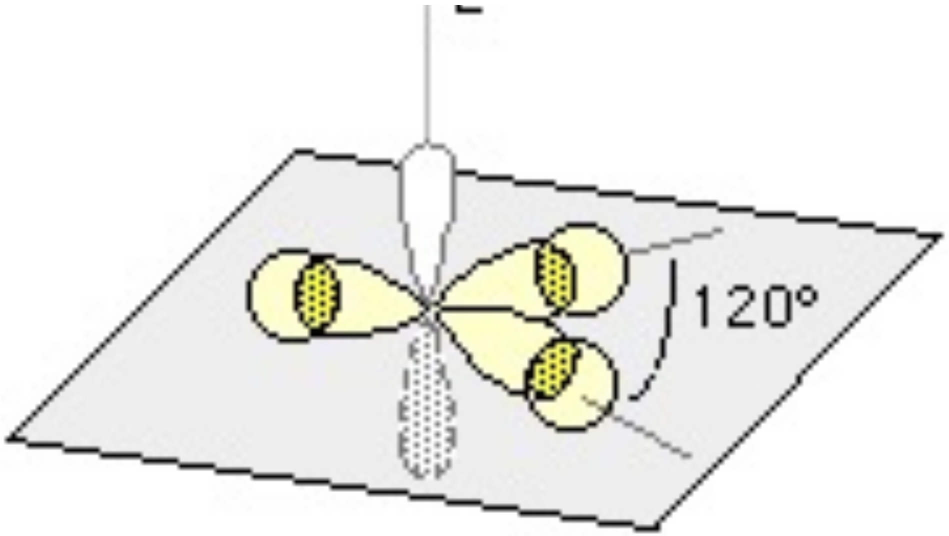
In sp² hybridization, orbitals 2s, $2p_x$ e $2p_y$ are combined forming three equivalent orbitals



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.

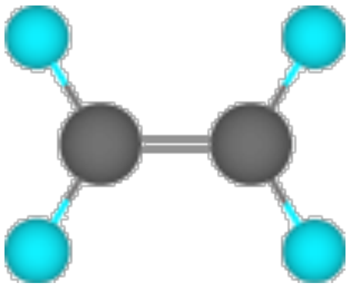


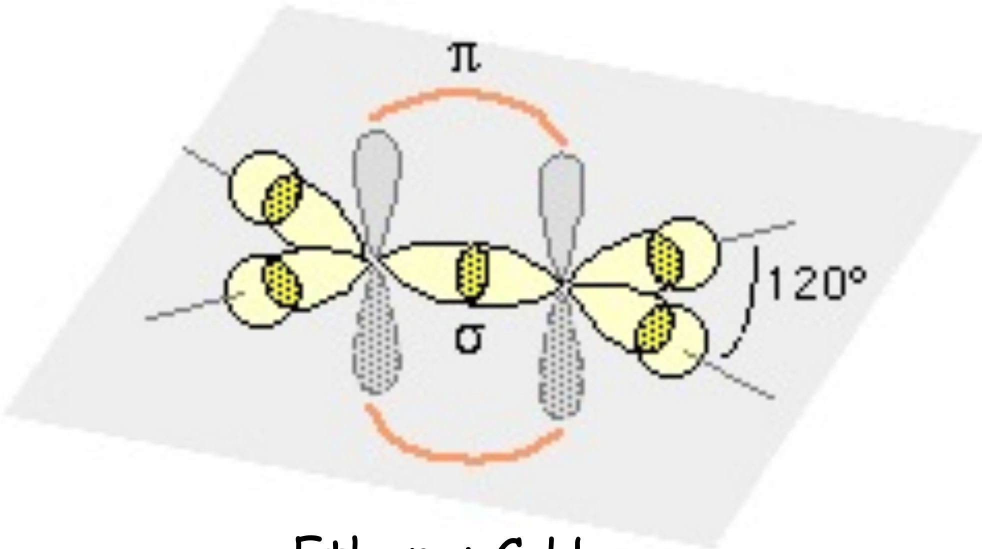


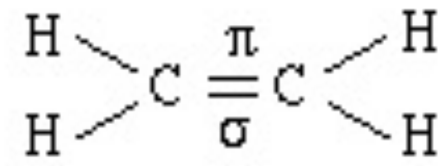
Sp^2 hybridization

The 3 coplanar orbitals can from 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.



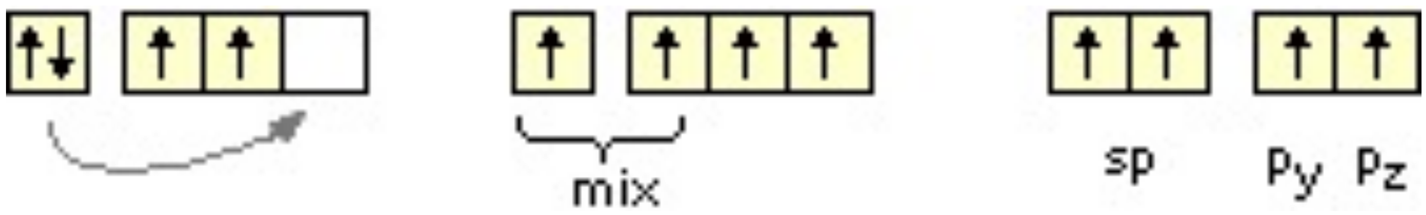




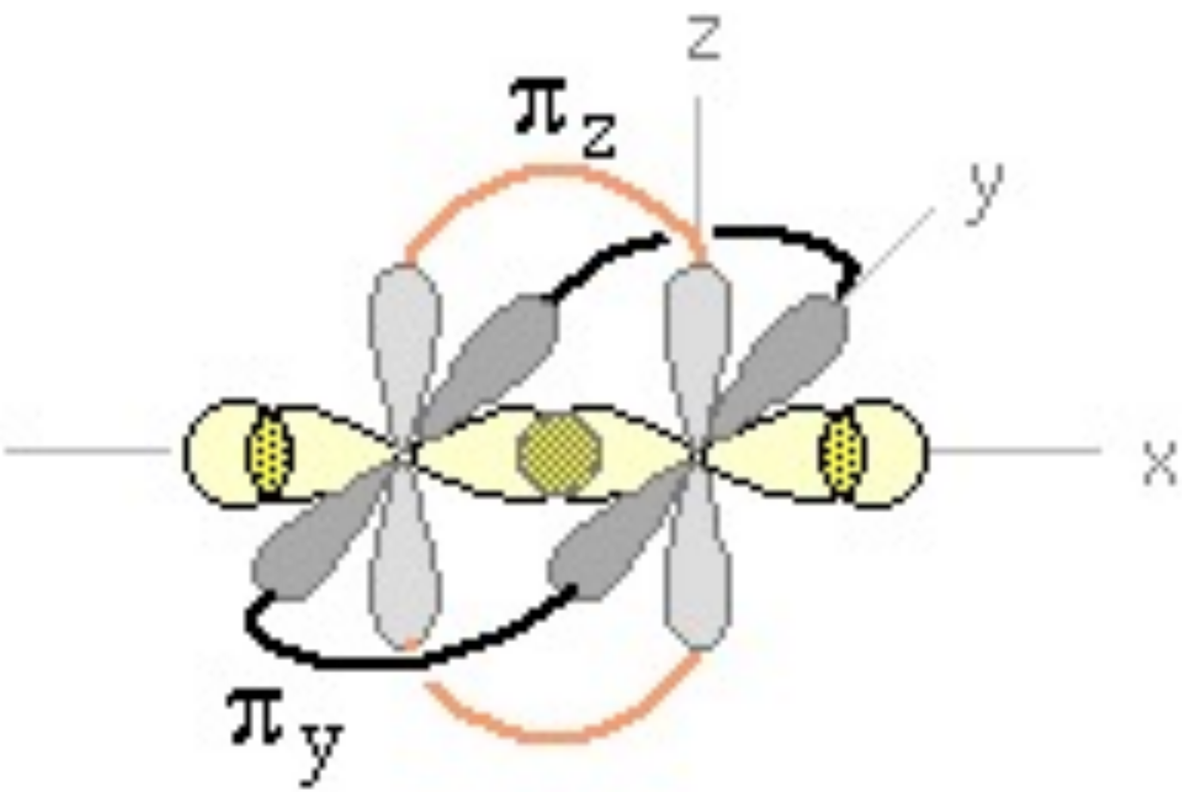
Ethene: C_2H_4

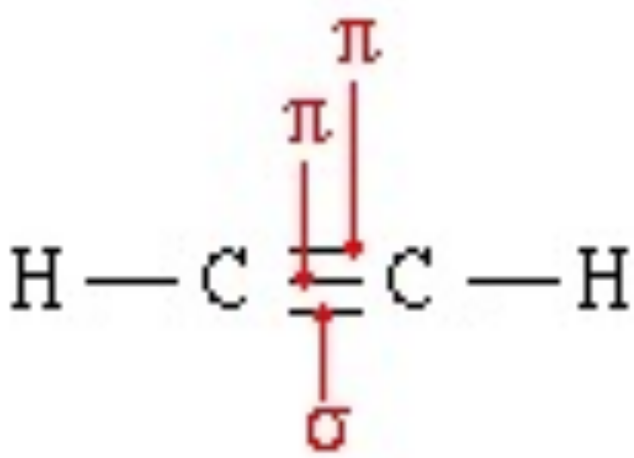
This is a characteristic of ALKENES, which are defined by having at least one double bond.

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 remining nt hybridized ones can form π bonds.



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

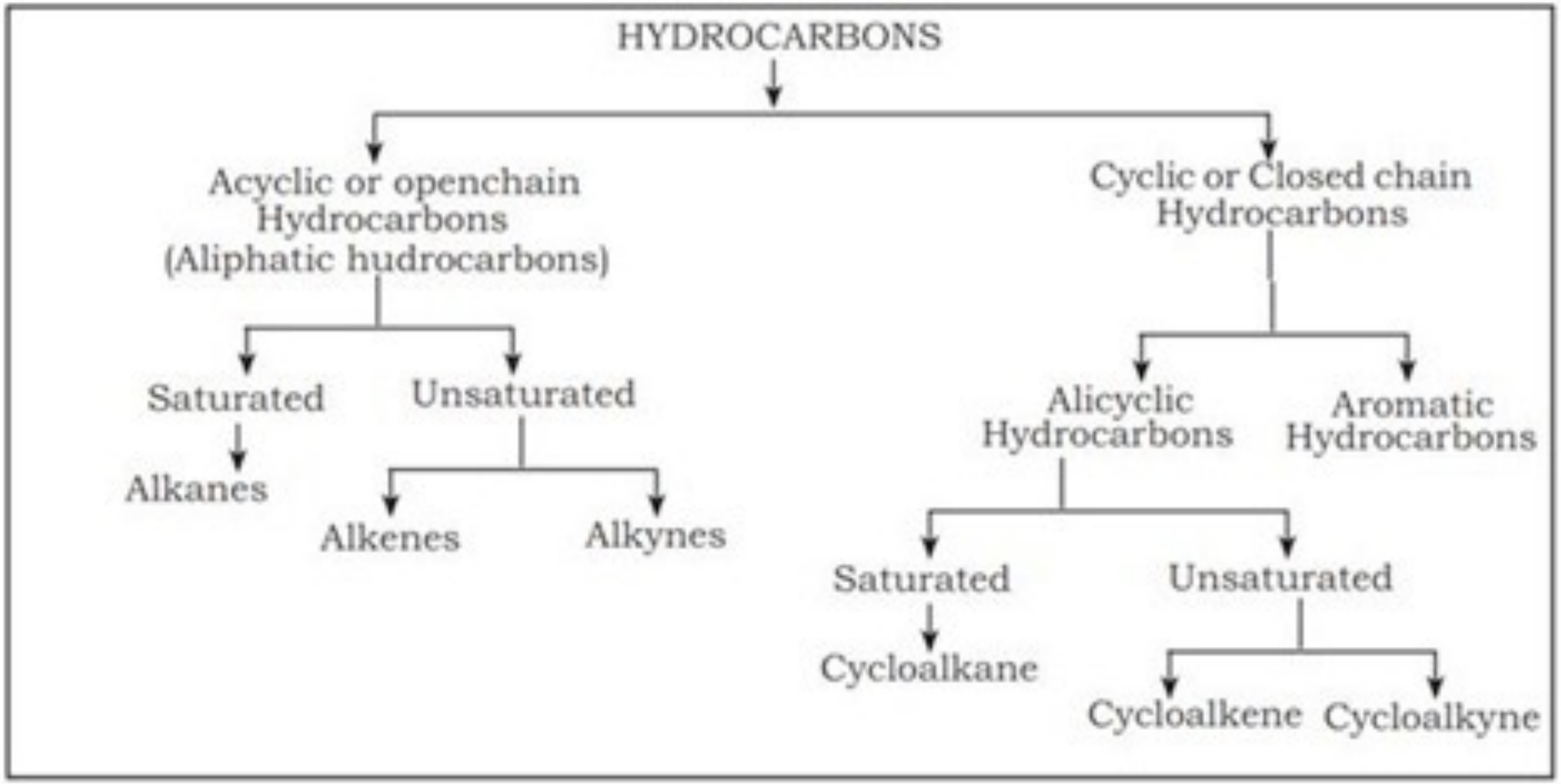




Ethyne (acetylene): C_2H_2

Hydrocarbon Classification

Compounds of carbon and hydrogen.



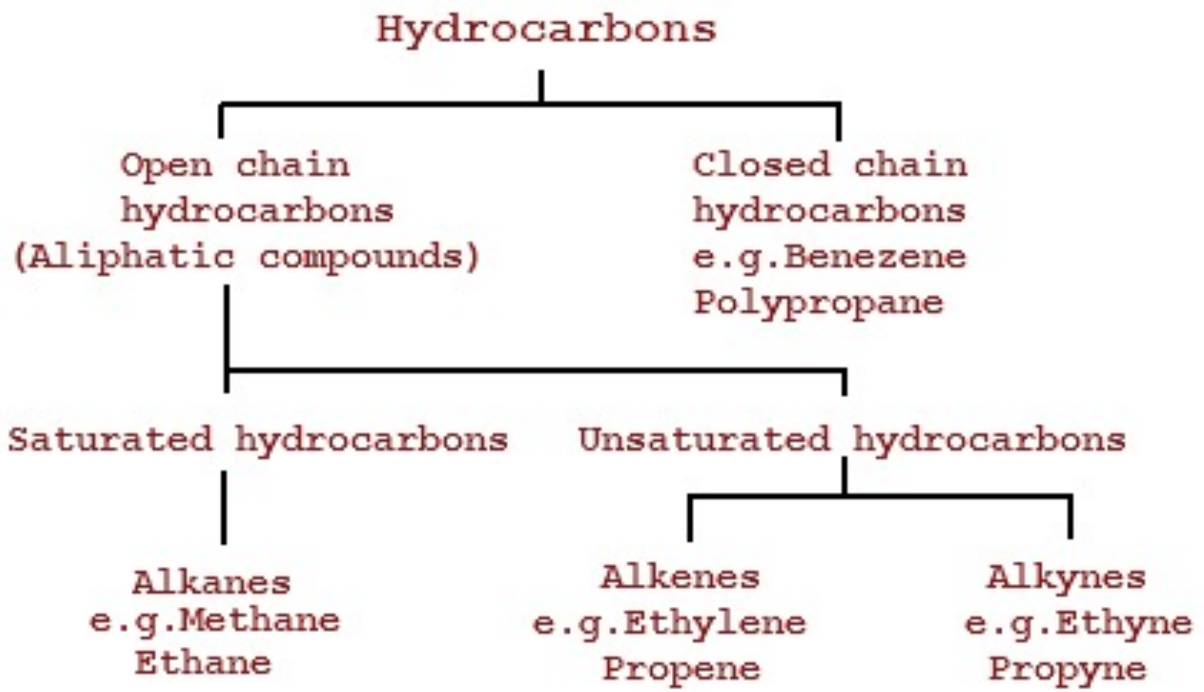
Hydrocarbons

1 Aliphatic open chain

2 Cyclic contain rings

3 Aromatic containing at least one benzene ring

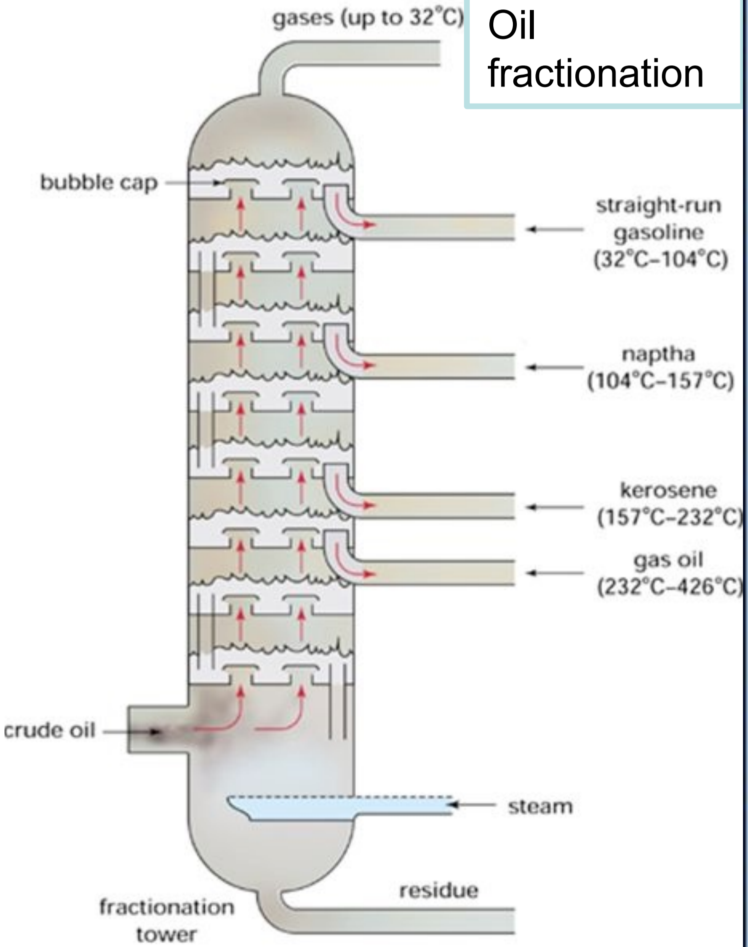
4 Heterocyclic rings with one or more atom different from carbon.

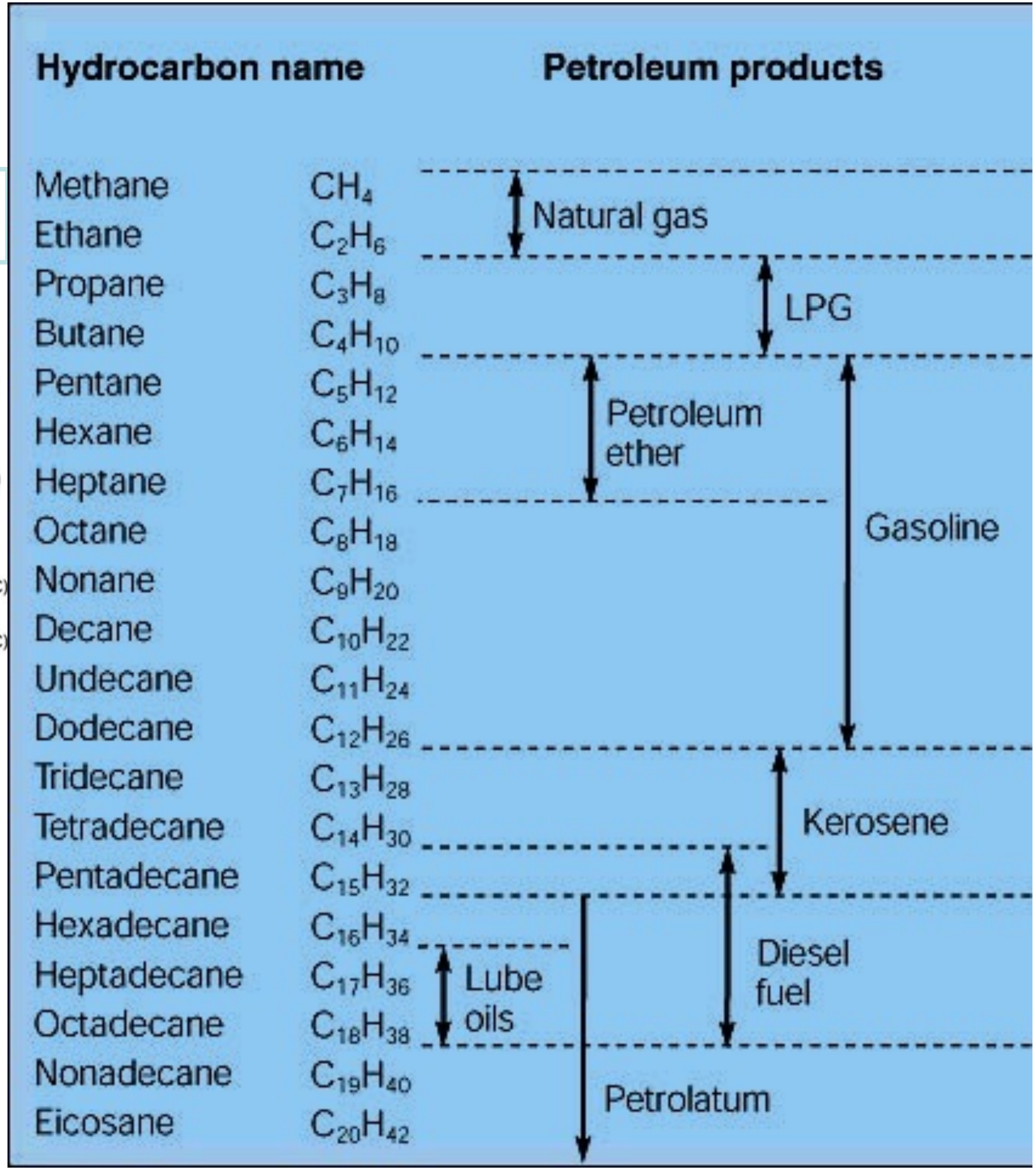


Hydrocarbons

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.

Oil fractionation





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, $CH_3(CH_2)_{n-1}H$

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]

[a]At the boiling point. [b]Under pressure. [c]For the supercooled liquid.

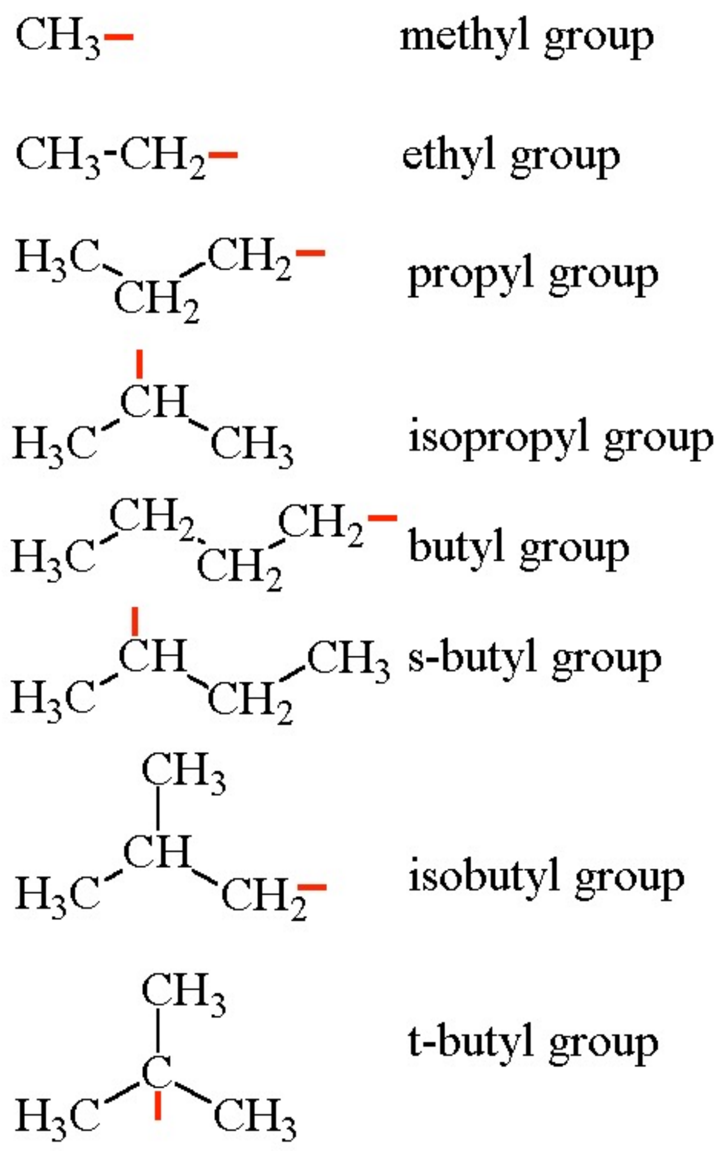
IUPAC Alkanes nomenclture

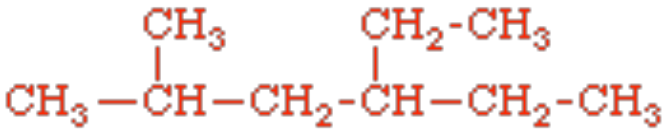
1. Choose the longest chain.
2. Consider the compound as a derivative, vith H atoms substituted by alkyl groups. [alkyl groups: groups wih a H less than the corresponding alkane. CH_3-, methyl; CH_3-CH_2-, ethyl; CH_3-CH_2-CH_2-, propyl; ec.]
3. Number the main chain atom in order to use the smallest 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_2H_6	Ethyl	$-C_2H_5$
3	Propane	C_3H_8	Propyl	$-C_3H_7$
4	Butane	C_4H_{10}	Butyl	$-C_4H_9$
5	Pentane	C_5H_{12}	Pentyl	$-C_5H_{11}$
6	Hexane	C_6H_{14}	Hexyl	$-C_6H_{13}$
7	Heptane	C_7H_{16}	Heptyl	$-C_7H_{15}$
8	Octane	C_8H_{18}	Octyl	$-C_8H_{17}$
9	Nonane	C_9H_{20}	Nonyl	$-C_9H_{19}$
10	Decane	$C_{10}H_{22}$	Decyl	$-C_{10}H_{21}$

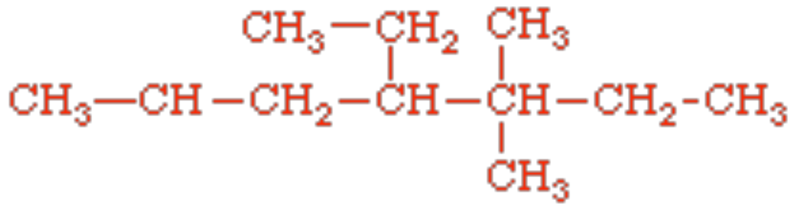
Names of alkyl groups

ALKYL GROUPS
(8 common ones)

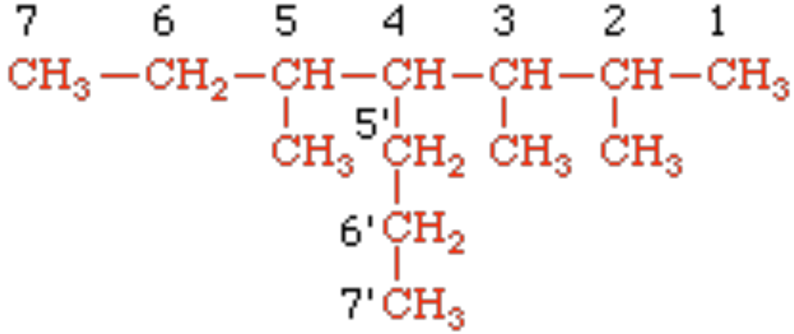




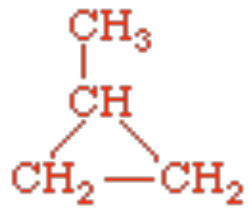
4-ethyl-2-methylhexane



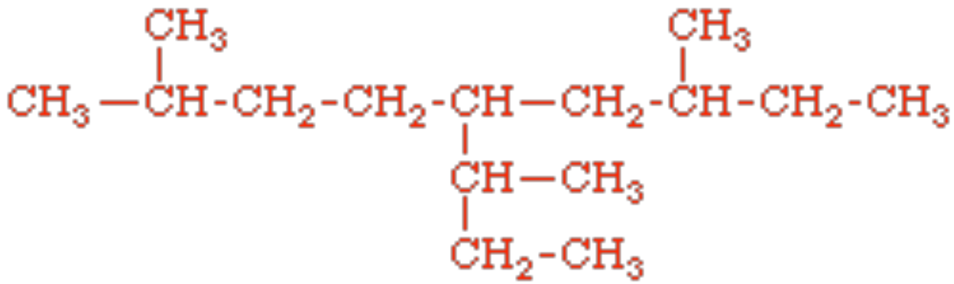
4-ethyl-3,3-dimethylheptane



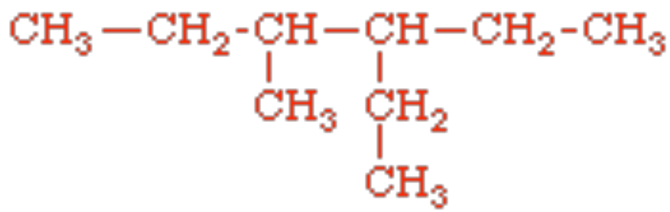
2,3,5-trimethyl-4-propylheptane
(NOT: 2,3-dimethyl-4-sec-butylheptane)



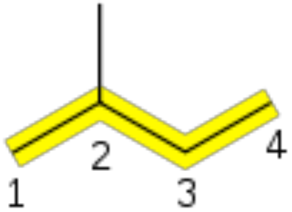
methylcyclopropane



5-sec-butyl-2,7-dimethylnonane

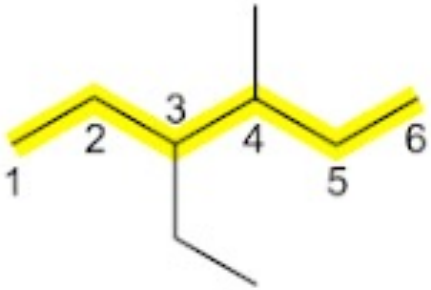


3-ethyl-4-methylhexane

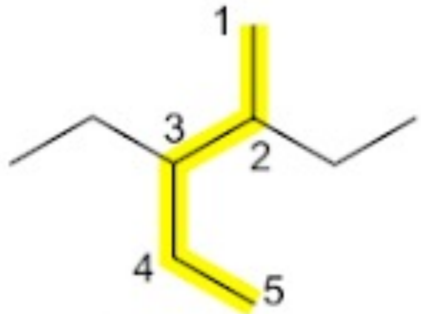


2-methylbutane
(correct numbering)

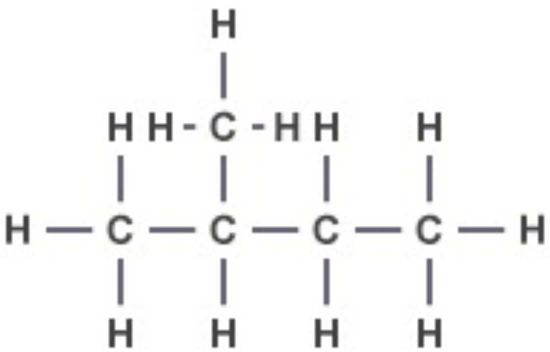
3-methylbutane
(incorrect numbering)



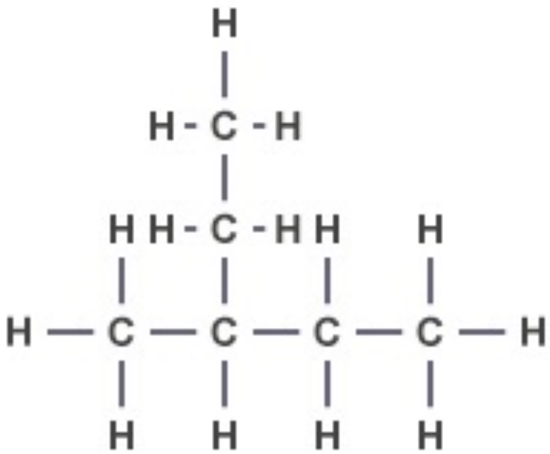
3-ethyl-4-methylhexane



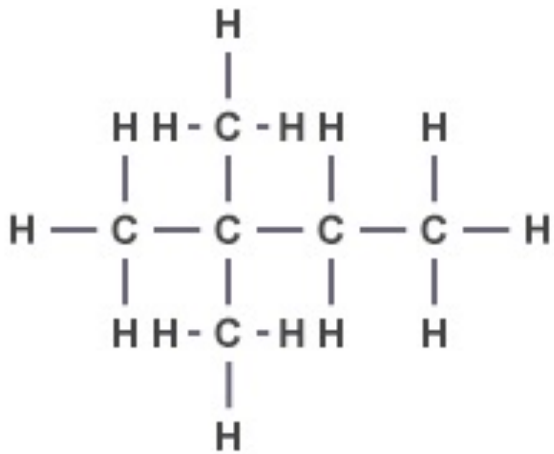
2,3-diethylpentane
(incorrect)



2-methylbutane



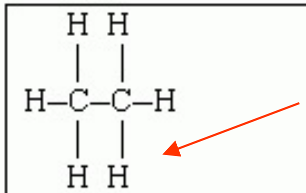
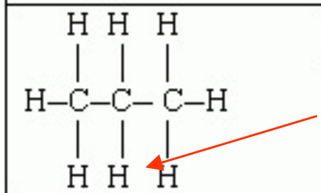
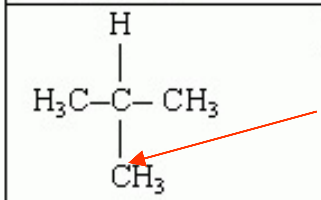
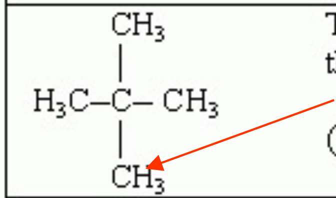
3-methylpentane
(not 2-ethylbutane)



2,2-dimethylbutane

Carbon atom classification

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

		Each C is attached to <u>one</u> other C atom; therefore, each is a <u>primary</u> C.
		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.)
Methyl-propane		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.) Note that I used a condensed formula here. It doesn't matter. It is up to you to count the C atoms.
Dimethyl-propane		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.)

Alkanes rections

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

Alogenation

$$CH_3\,CH_3 \xrightarrow[\text{Light, } 127°]{Br_2} CH_3\,CH_2Br$$

Oxidation

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

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

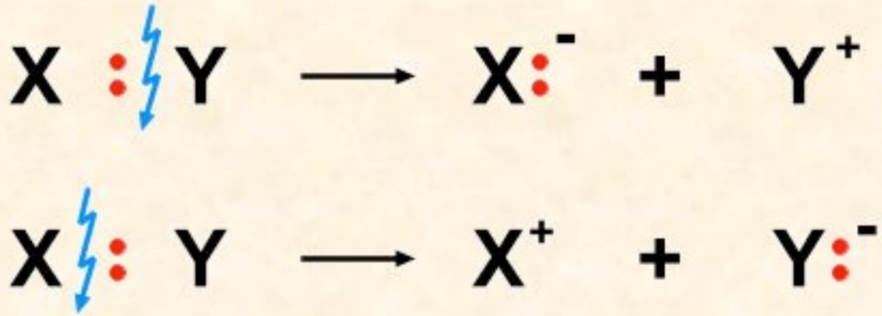
BREAKING COVALENT BONDS

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

UNEQUAL SPLITTING

produces **IONS**

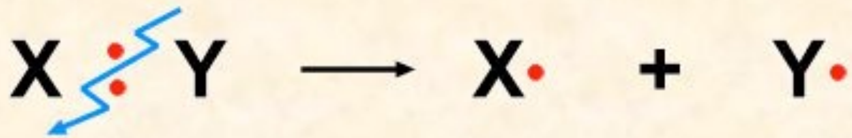
known as **HETEROLYSIS** or **HETEROLYTIC FISSION**



EQUAL SPLITTING

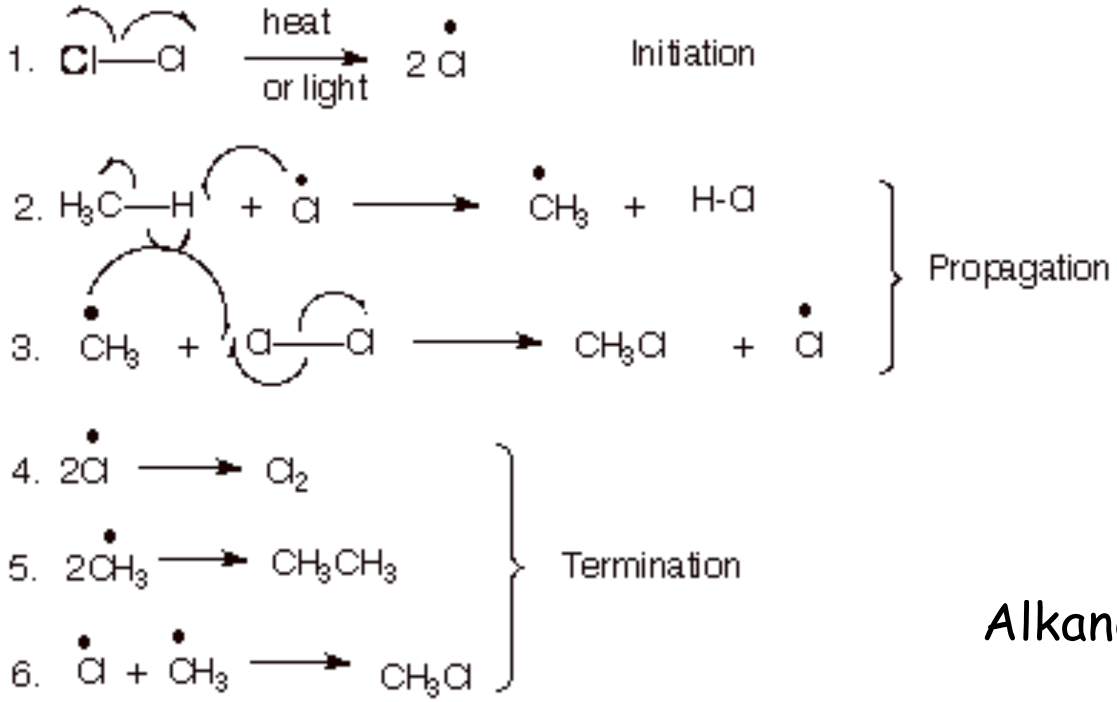
produces **RADICALS**

known as **HOMOLYSIS** or **HOMOLYTIC FISSION**

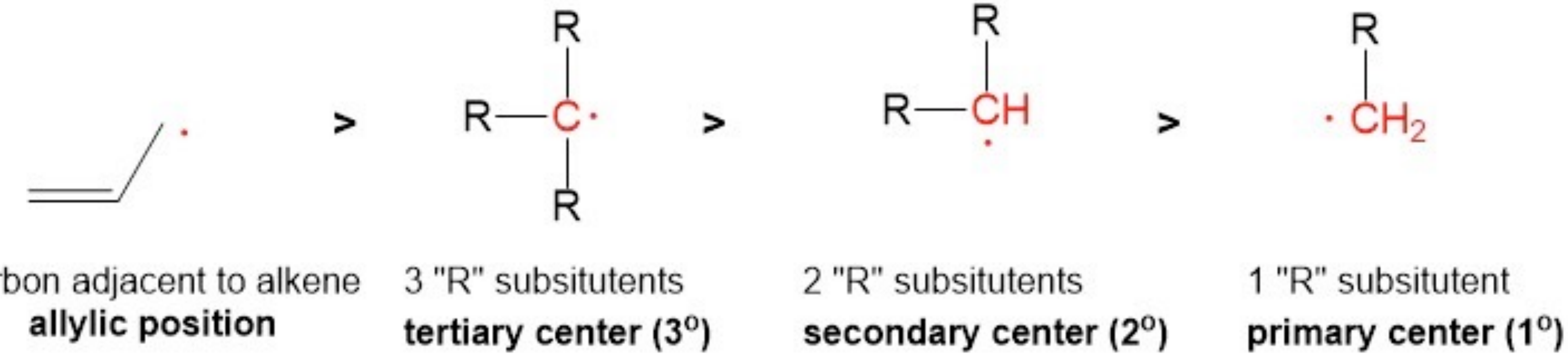


- If several bonds are present the weakest bond is usually broken first
- Energy to break bonds can come from a variety of energy sources - heat / light
- In the reaction between methane and chlorine either can be used, however...
- In the laboratory a source of UV light (or sunlight) is favoured.

Mechanism of radicalic halogenation (substitution)

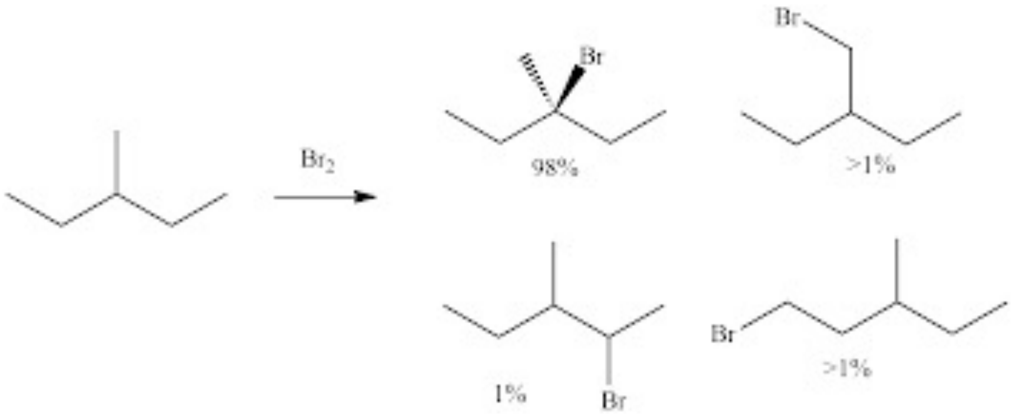


Alkane radicals stability



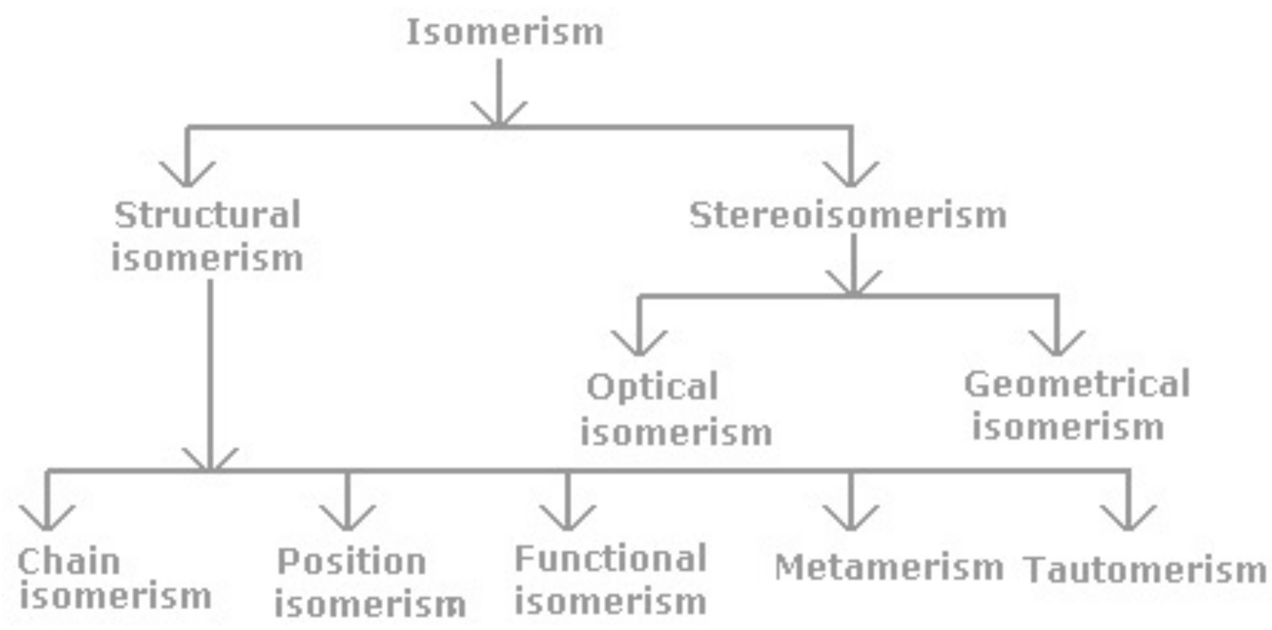
Carbon adjacent to alkene **allylic position** | 3 "R" subsitutents **tertiary center (3°)** | 2 "R" subsitutents **secondary center (2°)** | 1 "R" subsitutent **primary center (1°)**

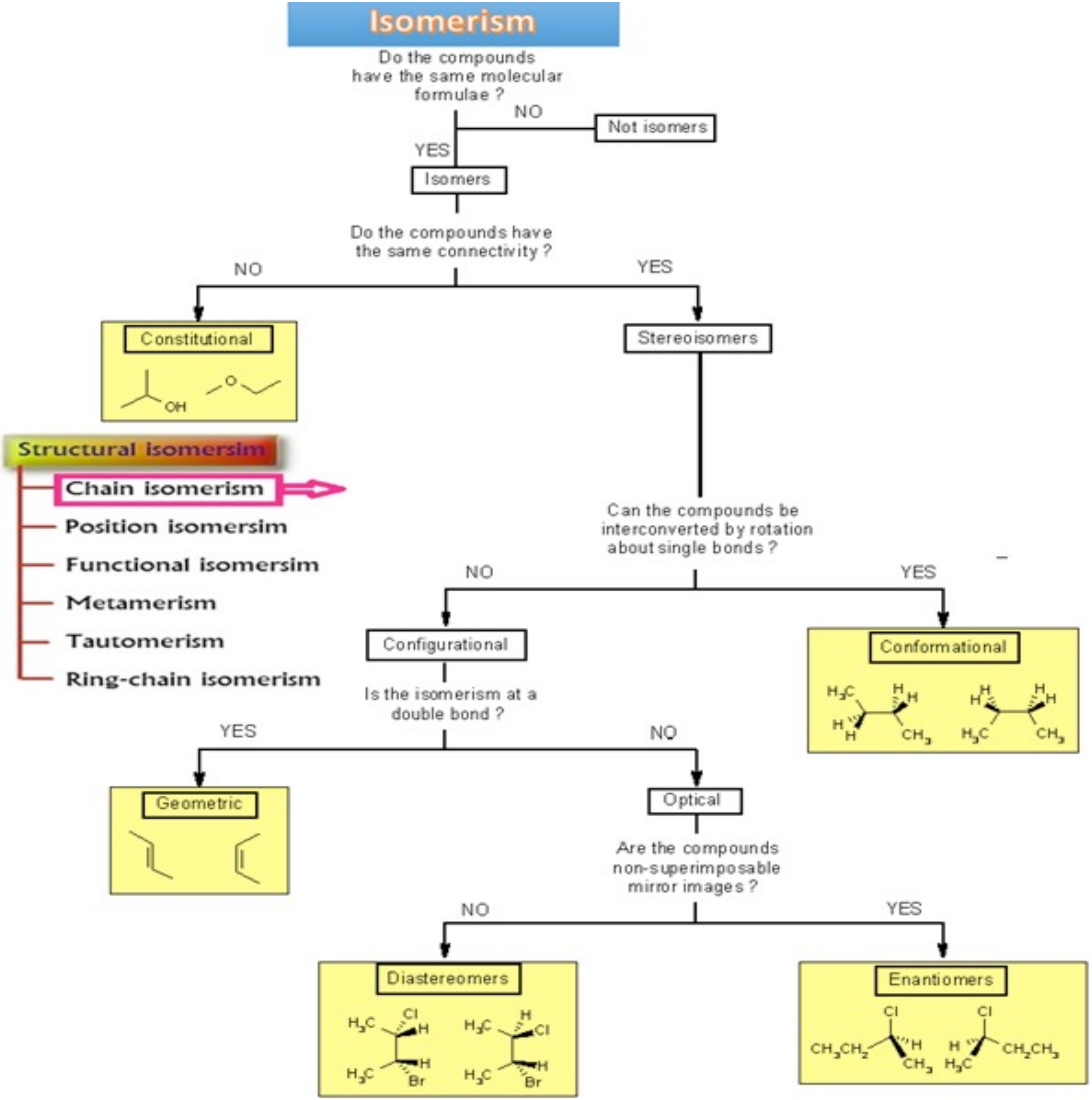
The product halogenated on tertiary C is more abundant, due to the relative stability of the radicals



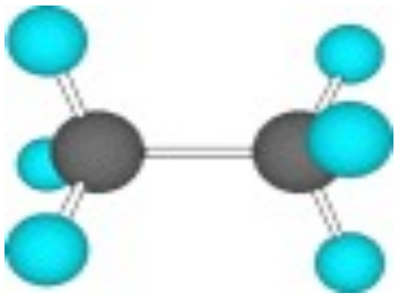
ISOMERISM

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.

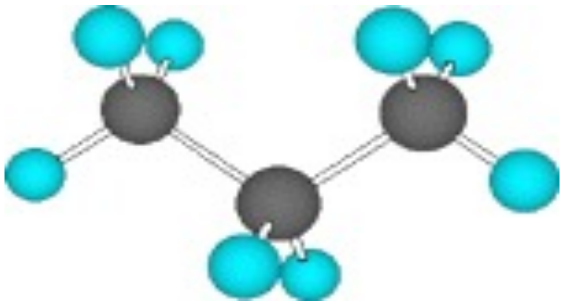



Isomerism
Do the compounds have the same molecular formulae ?
NO
Not isomers
YES
Isomers
Do the compounds have the same connectivity ?
NO
YES
Constitutional
OH
O
Stereoisomers
Structural isomersim
Chain isomerism
Position isomersim
Functional isomersim
Metamerism
Tautomerism
Ring-chain isomerism
Can the compounds be interconverted by rotation about single bonds ?
NO
YES
Configurational
Conformational
Is the isomerism at a double bond ?
YES
NO
Geometric
Optical
Are the compounds non-superimposable mirror images ?
NO
YES
Diastereomers
Enantiomers

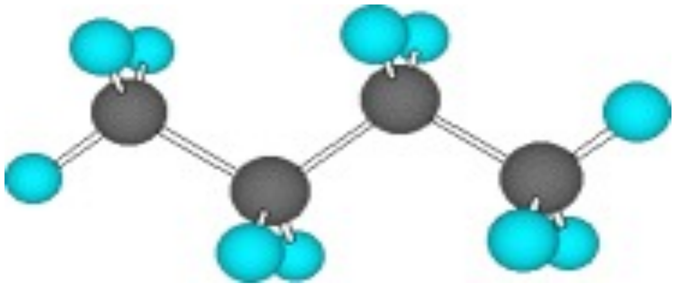
ALKANES



ethane (C_2H_6)



propane (C_3H_8)



butane (C_4H_{10}).

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

Butane has two isomers: *normal*butane (*n*-butane) and *iso*butane (or methylpropane).

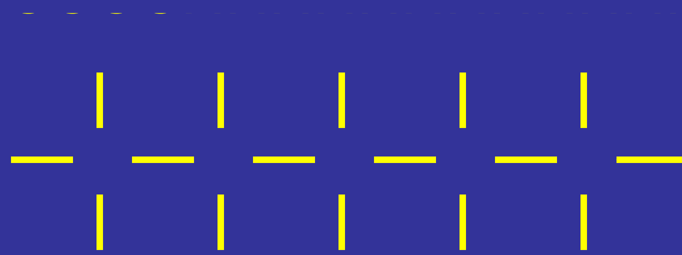
The larger the number of C atoms the larger the number of isomers:

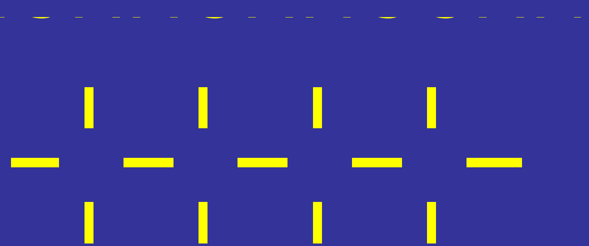
C_4H_{10} -> 2 isomers
C_5H_{12} -> 3 isomers
C_6H_{14} -> 5 isomers
C_7H_{16} -> 9 isomers
C_8H_{18} -> 18 isomers
C_9H_{20} -> 35 isomers
.....
$C_{40}H_{82}$ -> 62.491.178.805.831 isomers

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

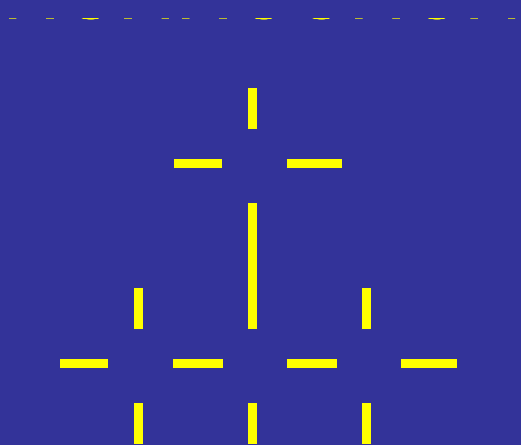
Isomerism of alkanes:

How many C_5H_{12}?

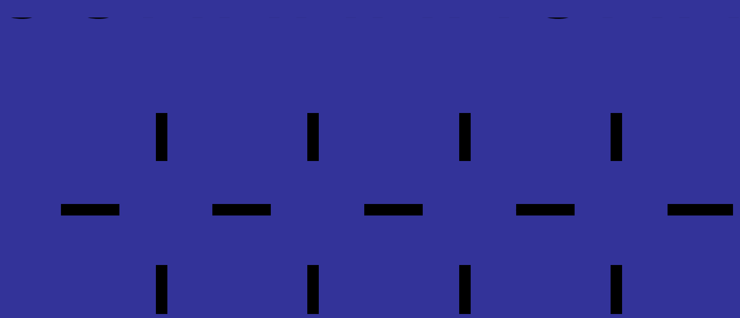


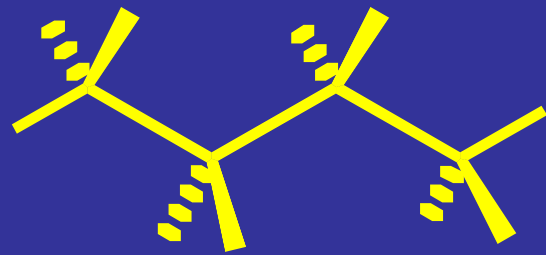


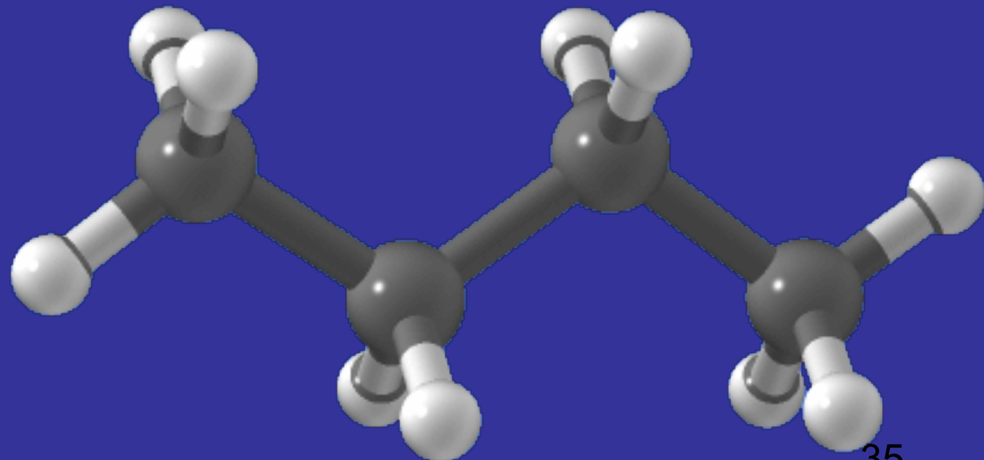
butane (C_4H_{10})



Butane = C_4H_{10}, $CH_3CH_2CH_2CH_3$

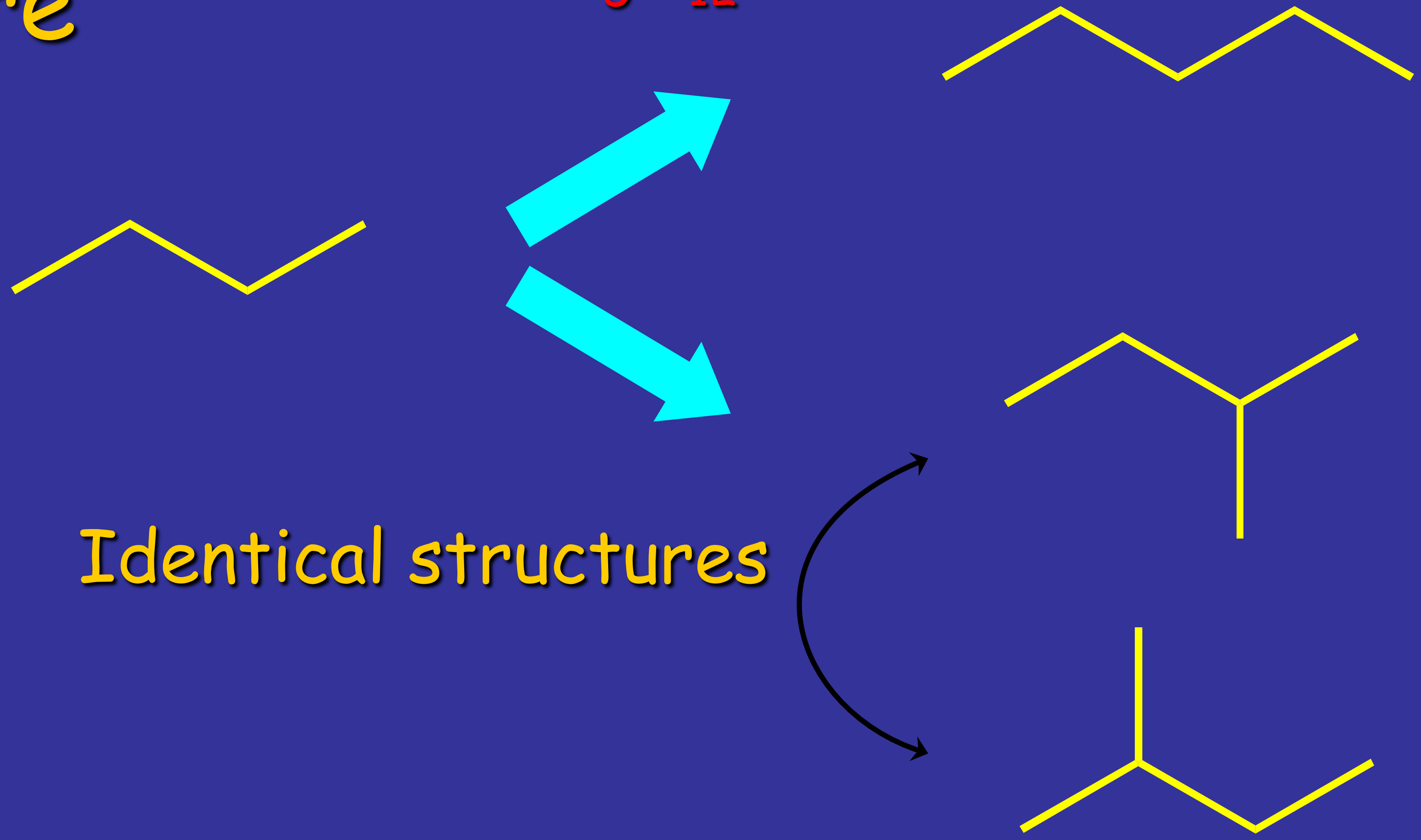


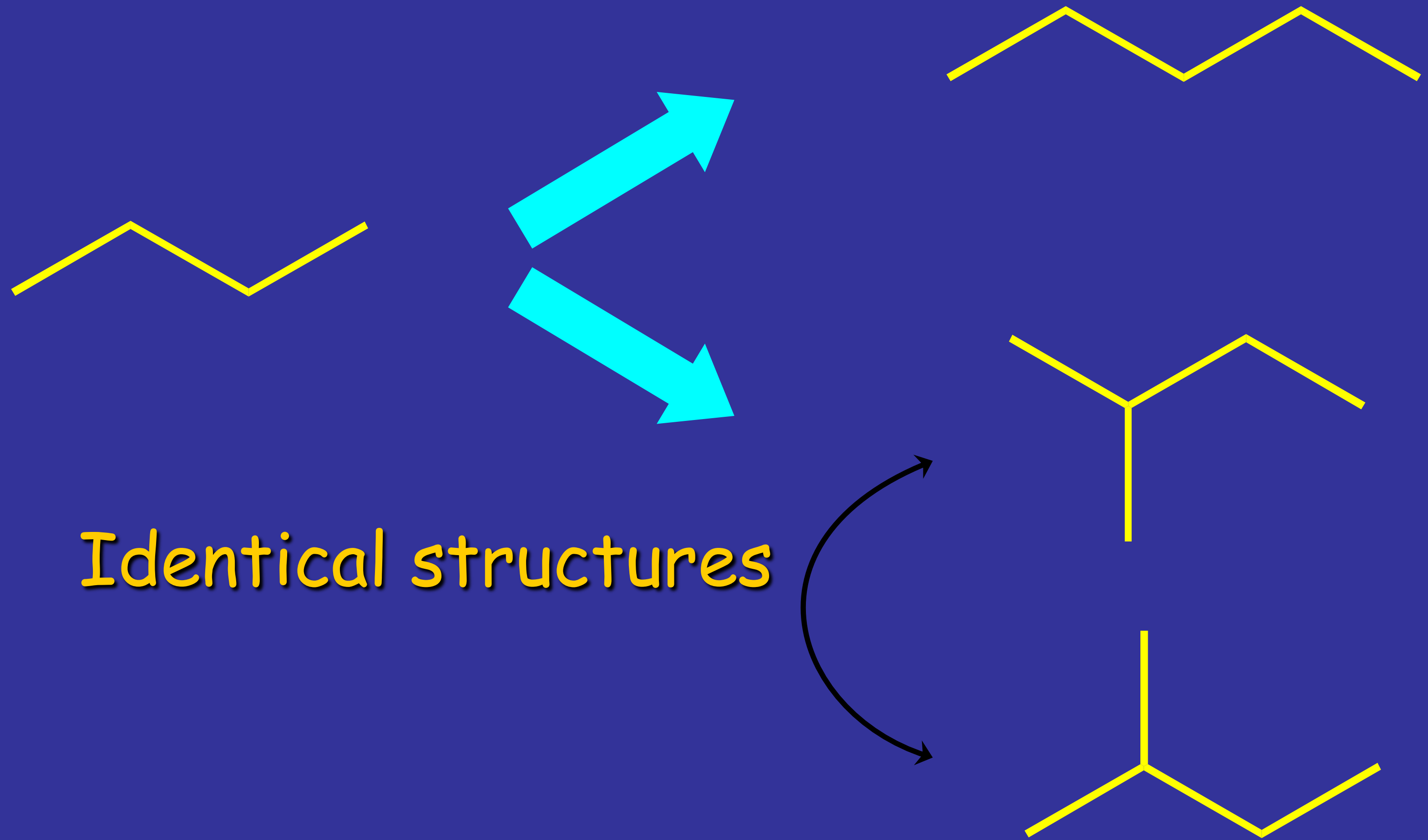




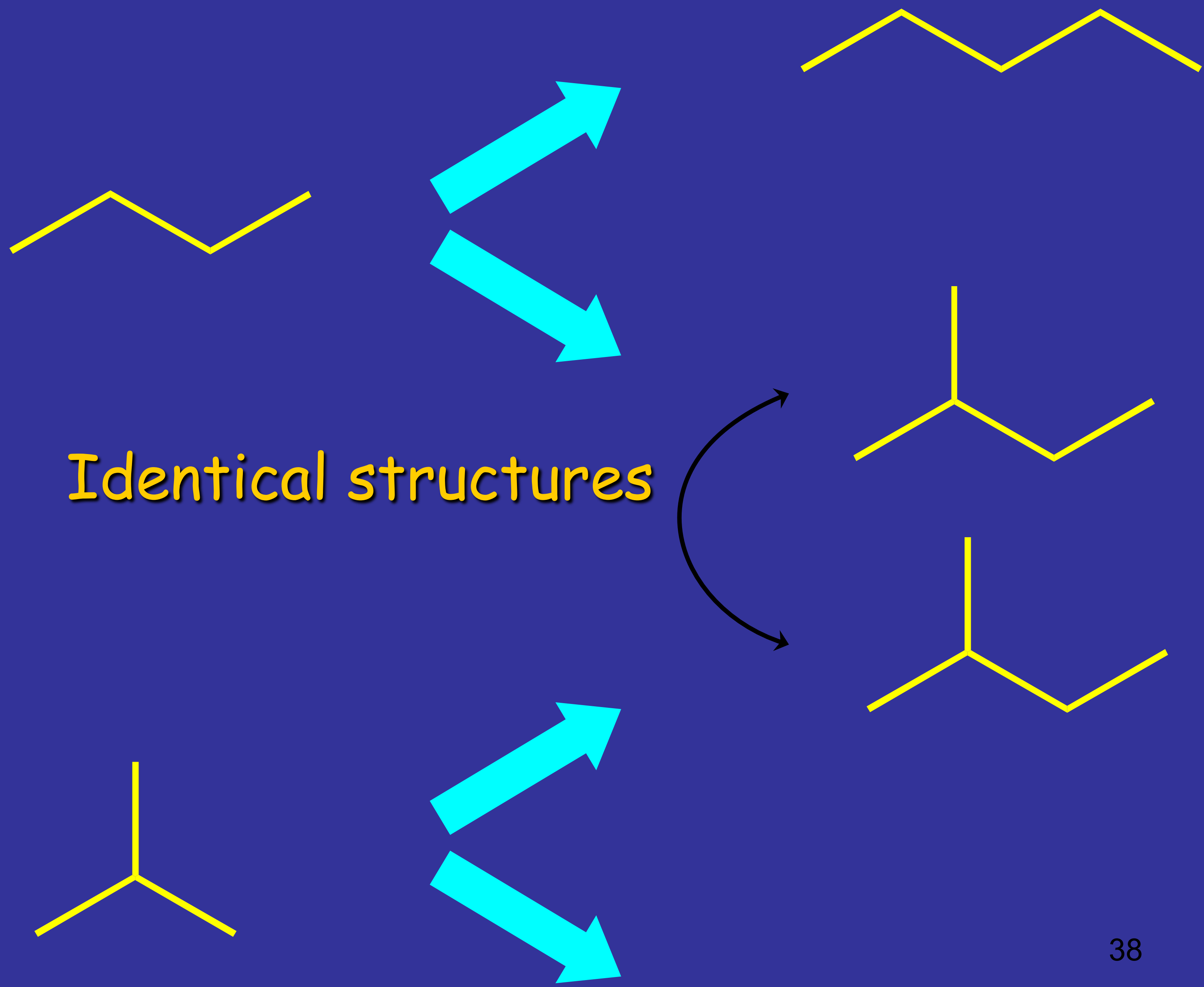
Simplified structure

How many isomers for C_5H_{12}?

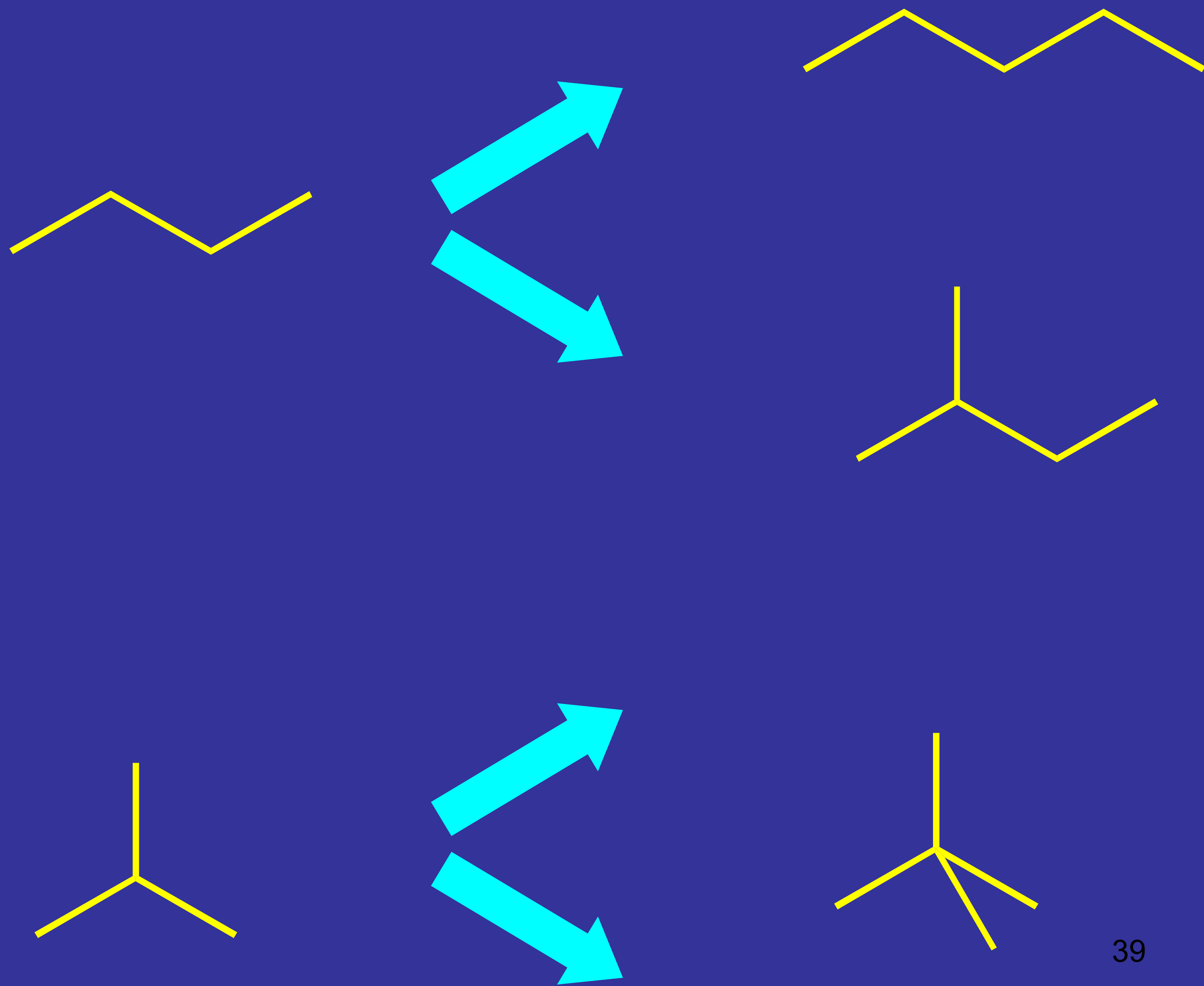



Identical structures

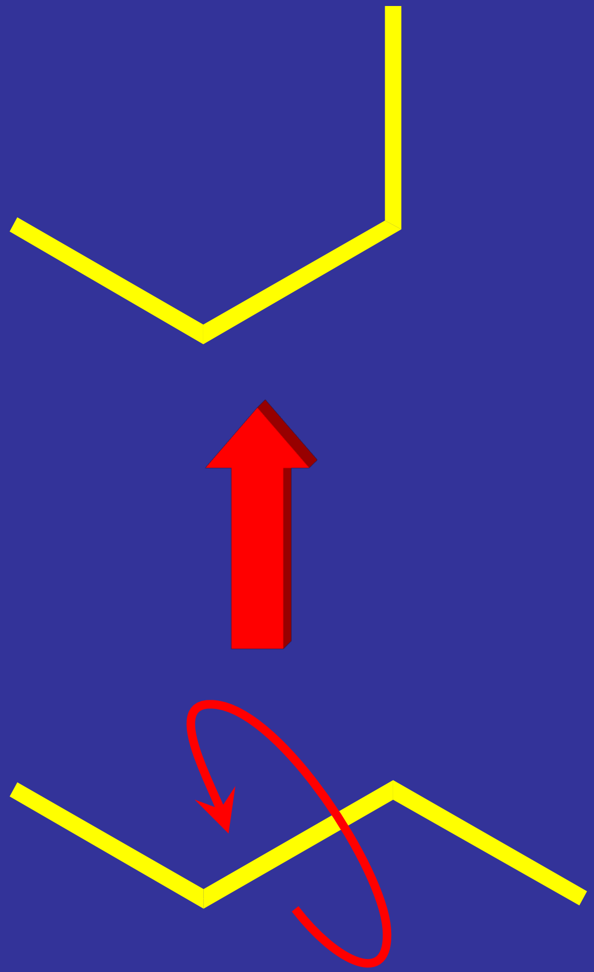
Isomers of alkanes: How many C_5H_{12}?

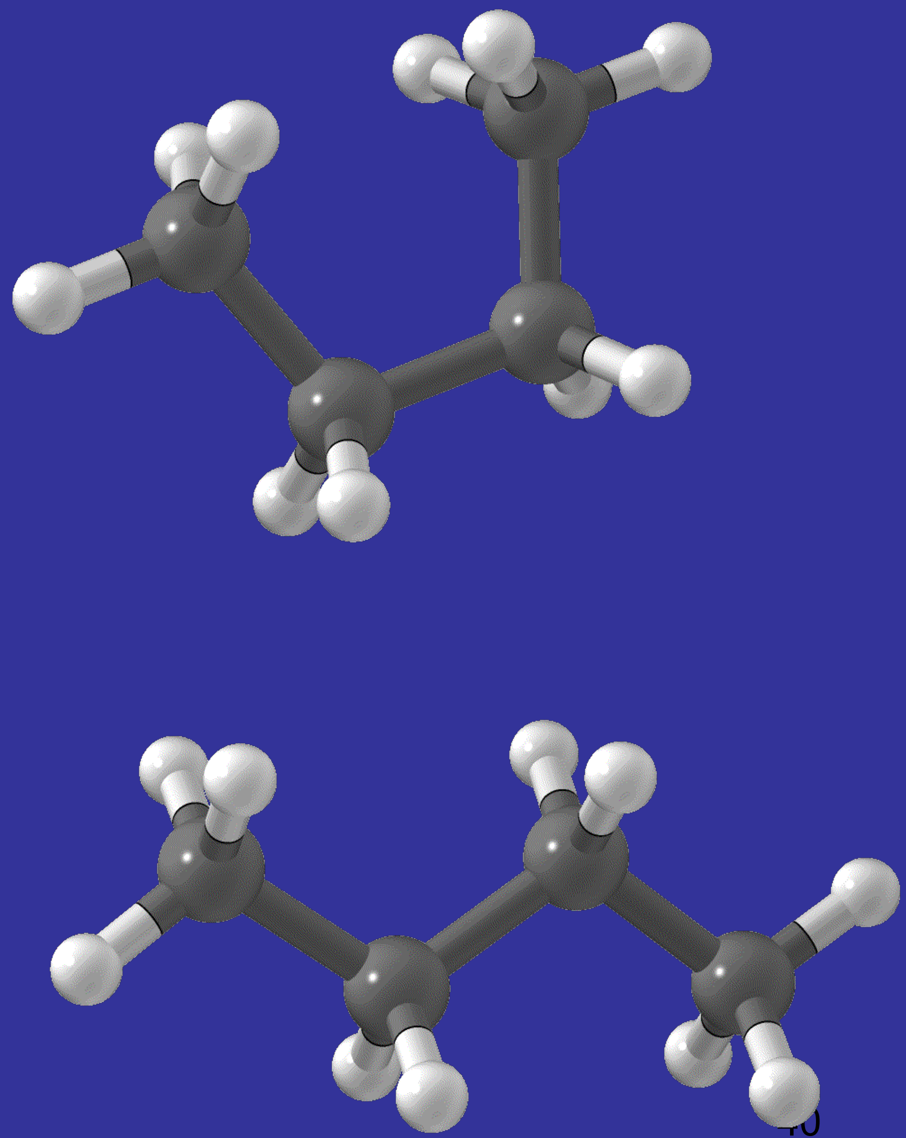


Isomers of alkanes: How many C_5H_{12}?

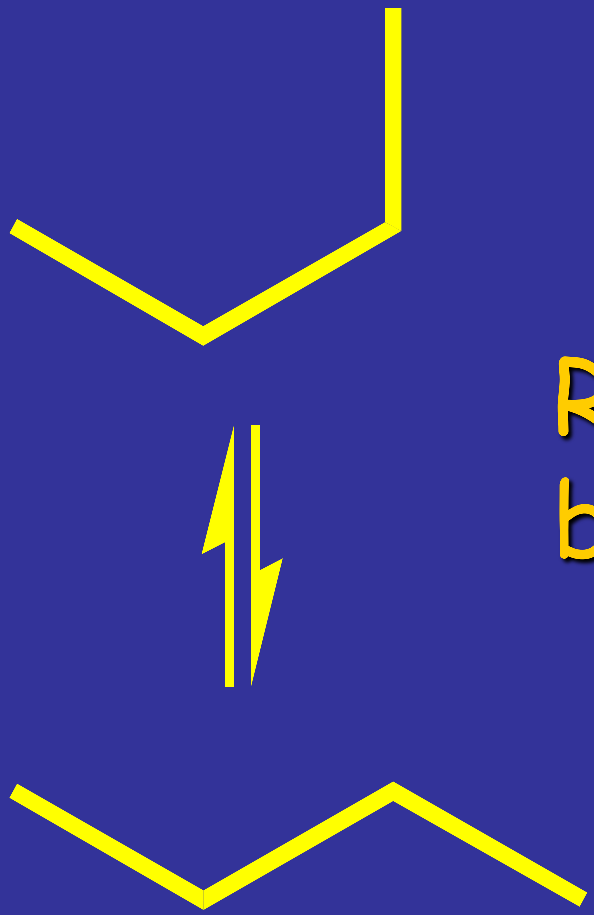


Butane, bond rotation



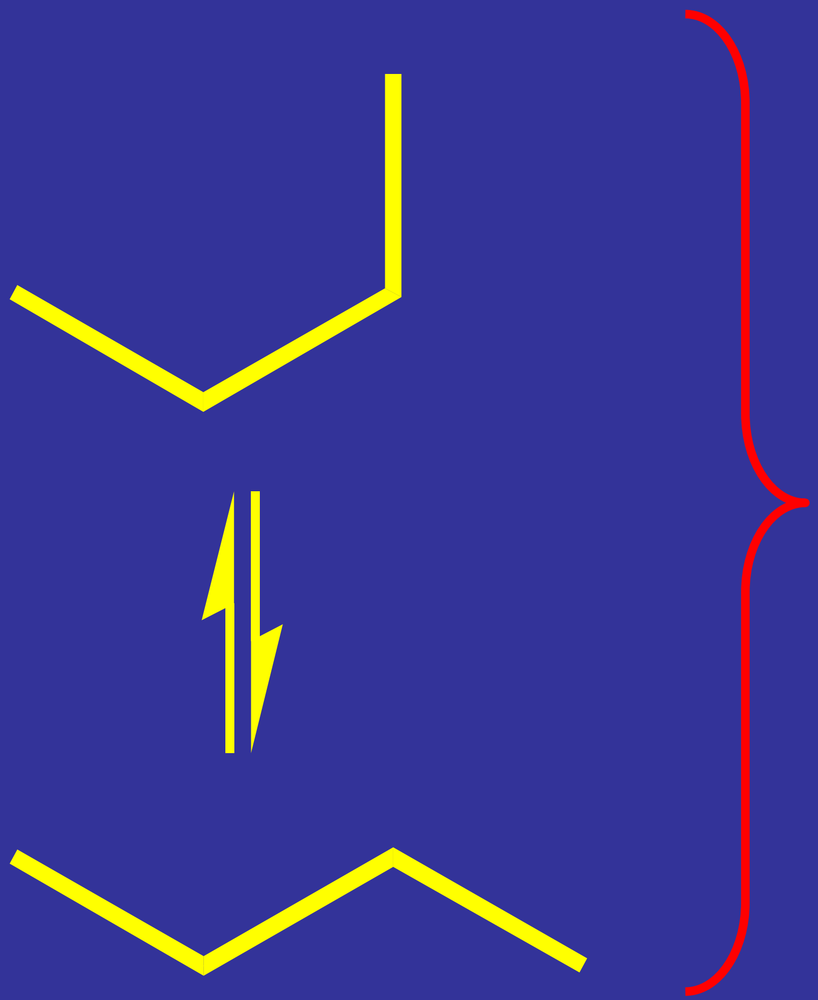


Butane, bond rotation



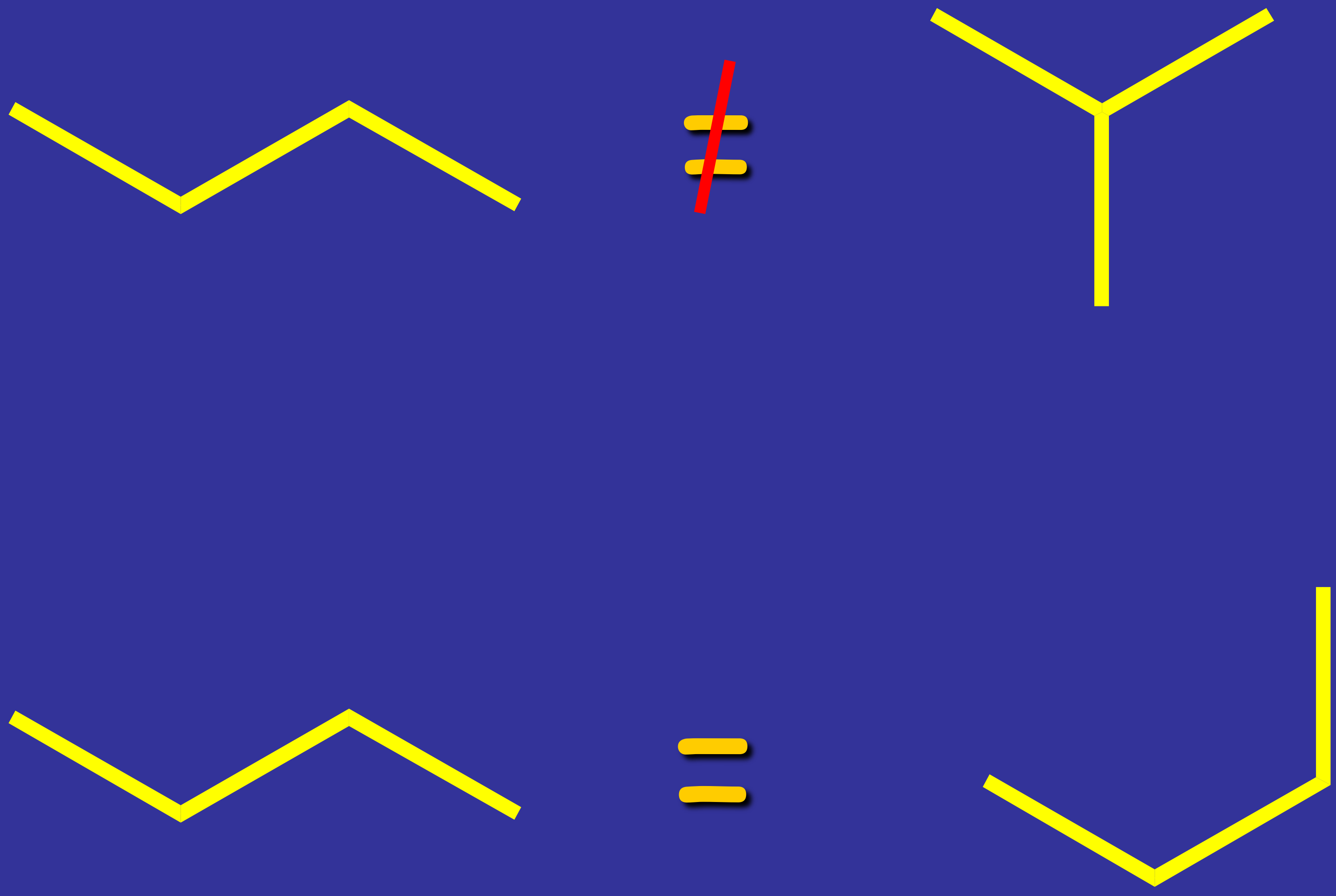
Rotation around single bonds is fast.

Butane, bond rotation



= butane

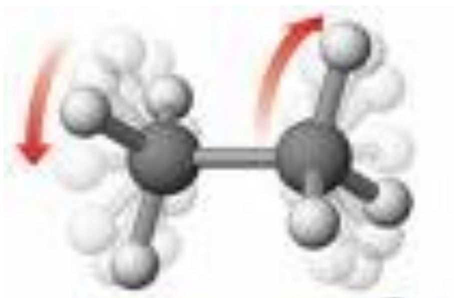
Isomers of C_4H_{10}.

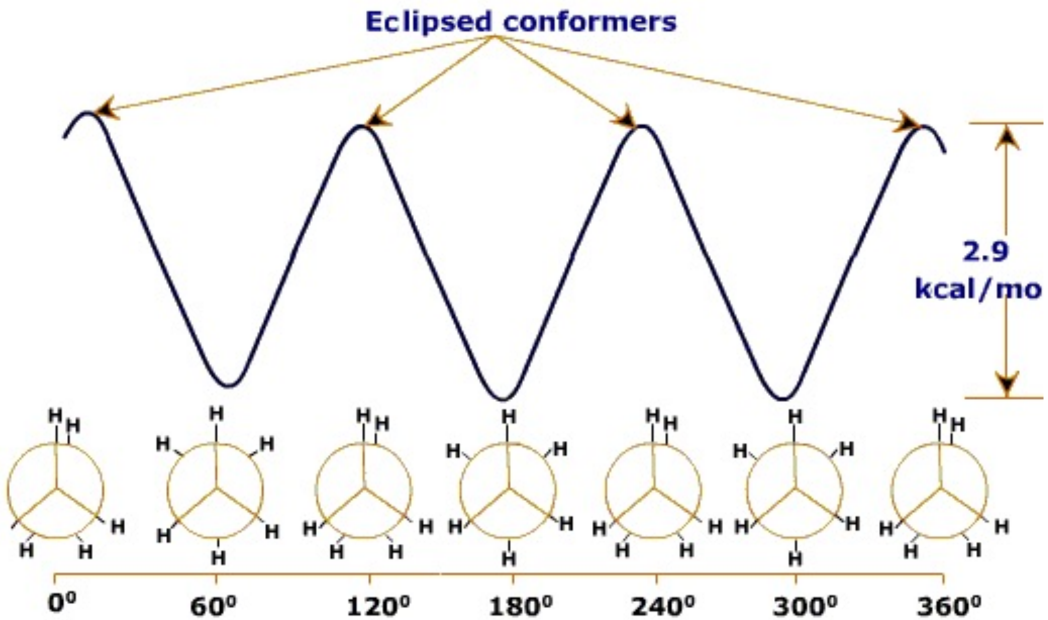


Stereoisomerism

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

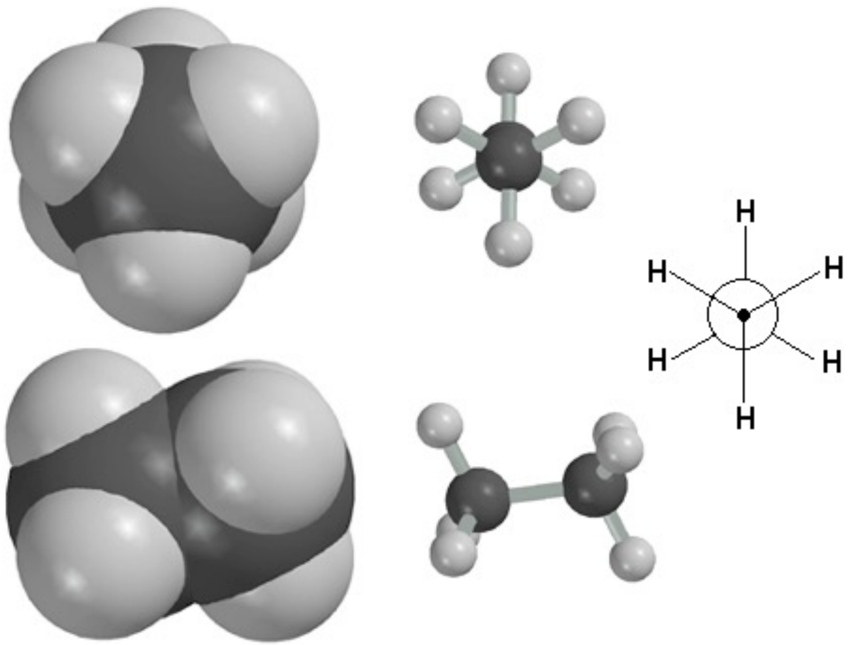
The σ bond can rotate→ the structure of ethane can assume al conformations from eclipsed to staggered.



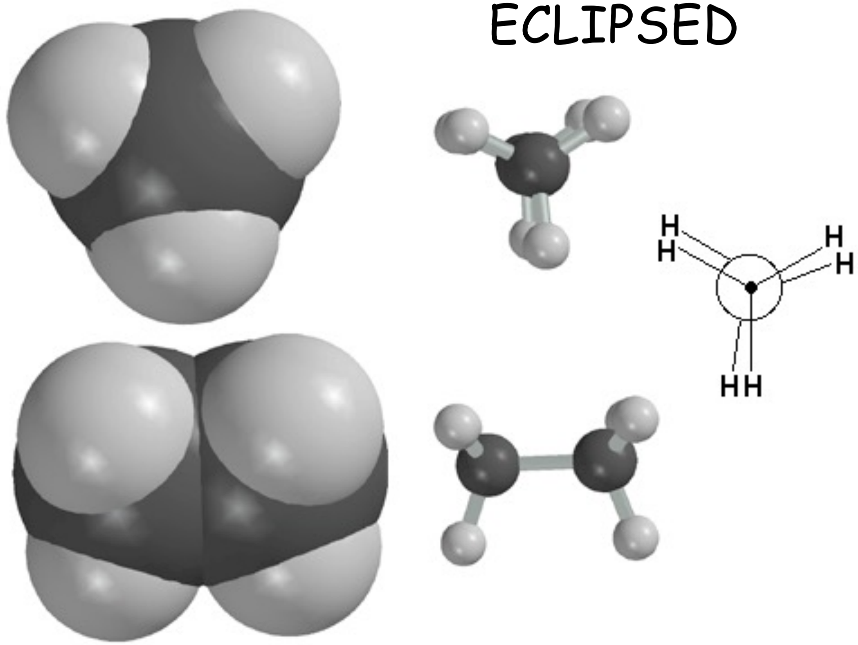


The staggered conformation is more stable by 2.9 kcal/mole

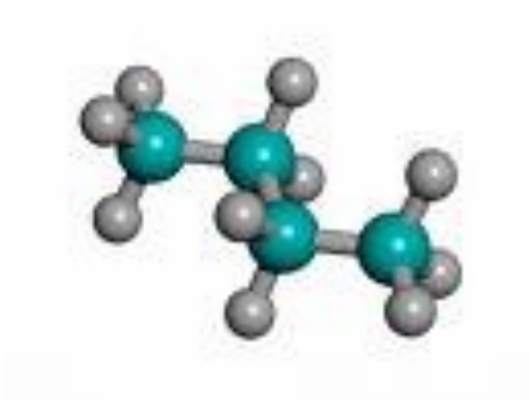
STAGGERED

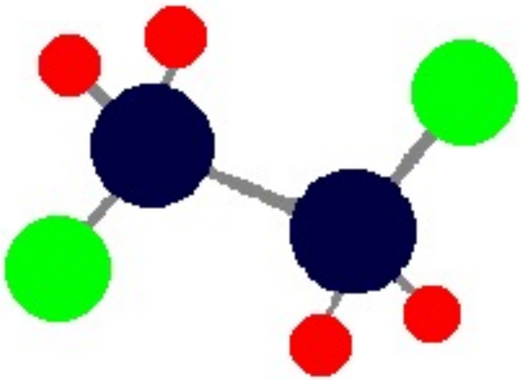


ECLIPSED

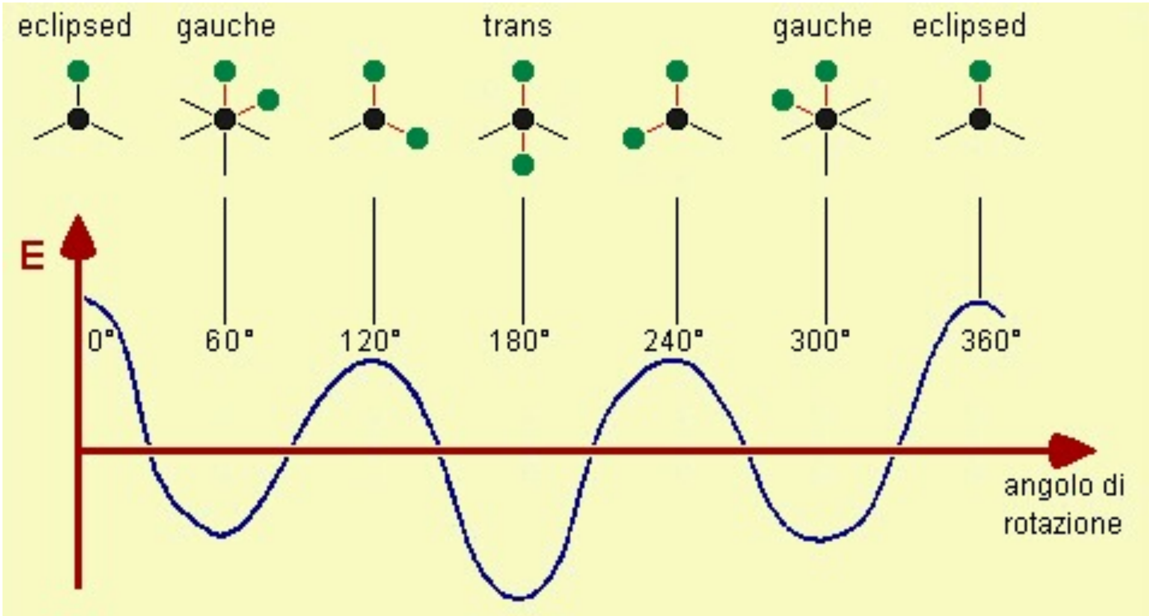


For molecules such as butane or 1,2 dichloroethane one finds relative and absolute minima.



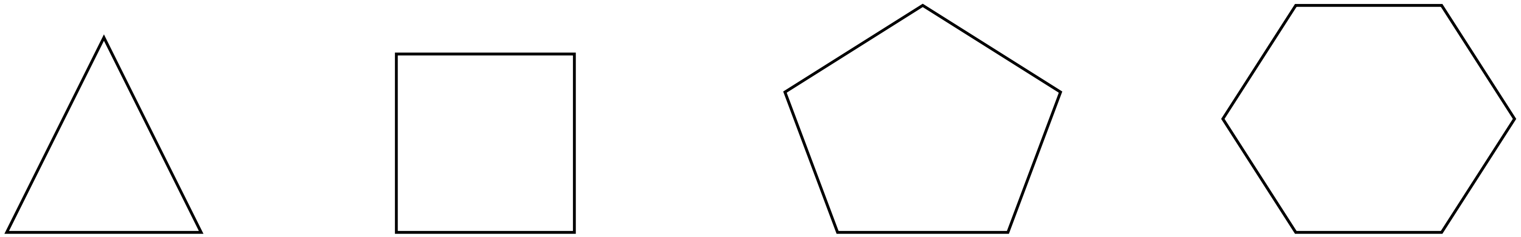


1,2-dichloroethane



CICLOALKANES

These are saturated hdrocarbons that have a closed chain.



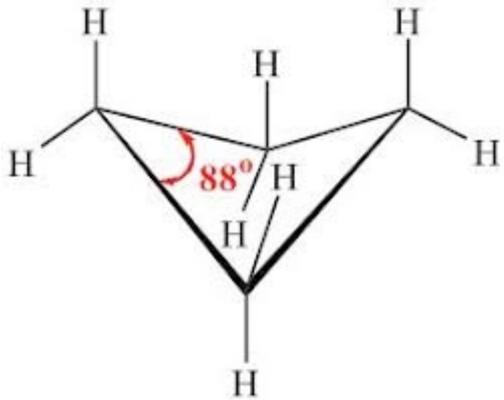
ciclopropane ciclobutane ciclopentane cyclohexane

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.

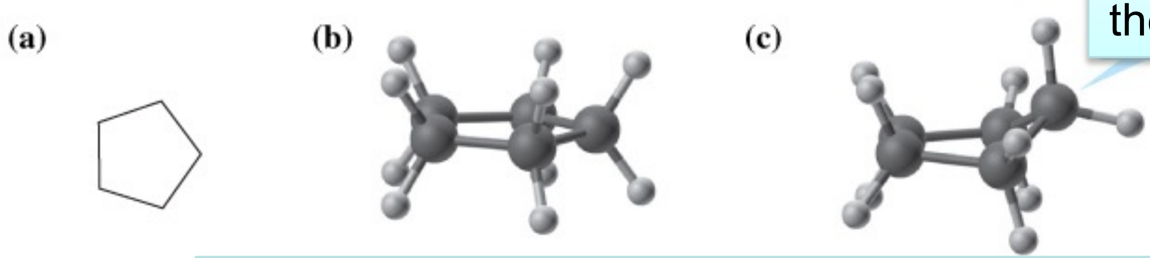
• *for a sp³carbon, the deviation from a tetrahedral geometry causes an angular tension.*

• *A couple of sp³ carbons is more stable if their conformation is staggered.*



cyclobutane

cyclopentane

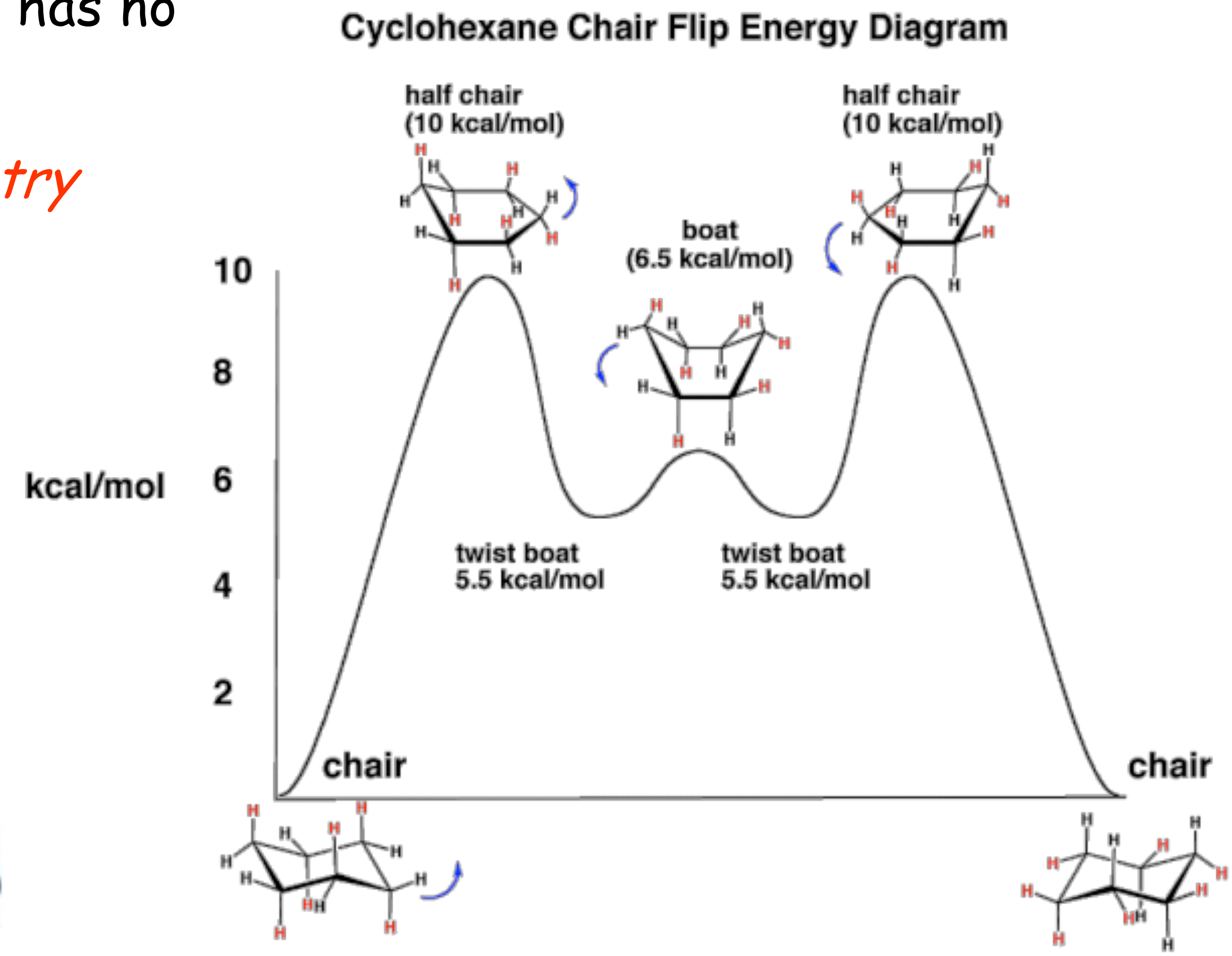


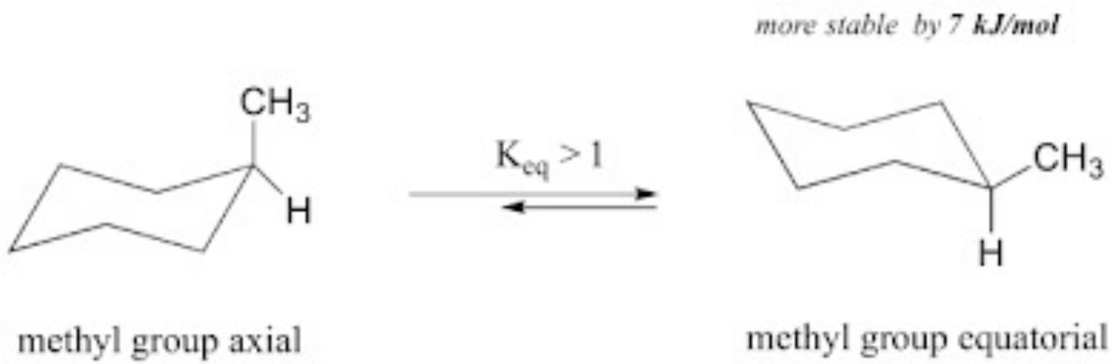
Folding partially relieves the angular tension

Planar conformation folded ("envelope") conformation

The "chair" conformation has no tension since *it has tetrahedral geometry and staggered conformation.*

Axial and equatorial

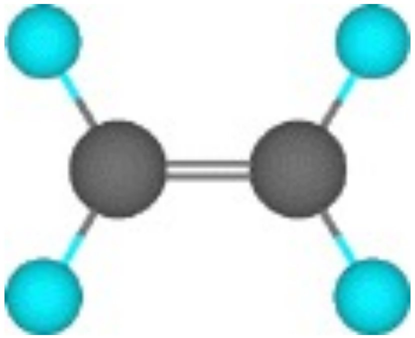




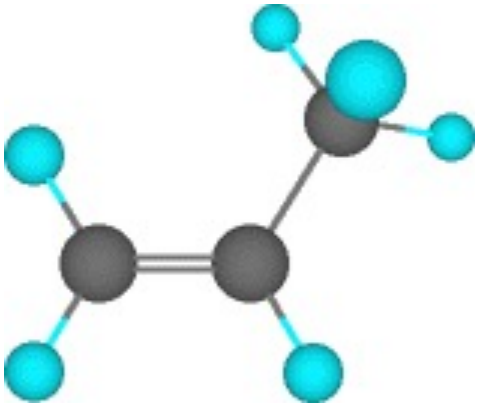
Insaturated hydrocarbons: **ALKENES**

Alkenes have at least a double π bond

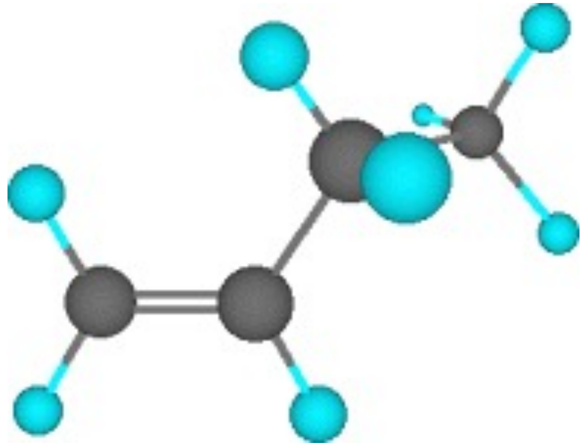
Their name has the suffix -ENE



Ethene
C_2H_2



Propene
(C_3H_6)

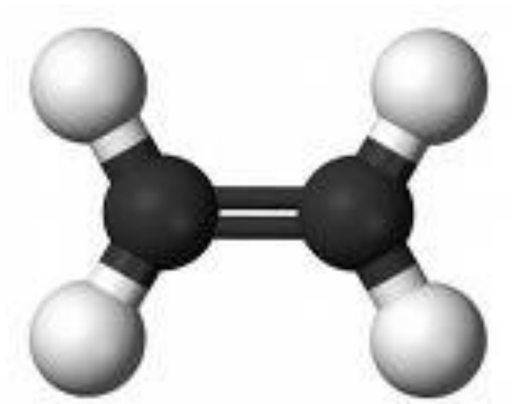


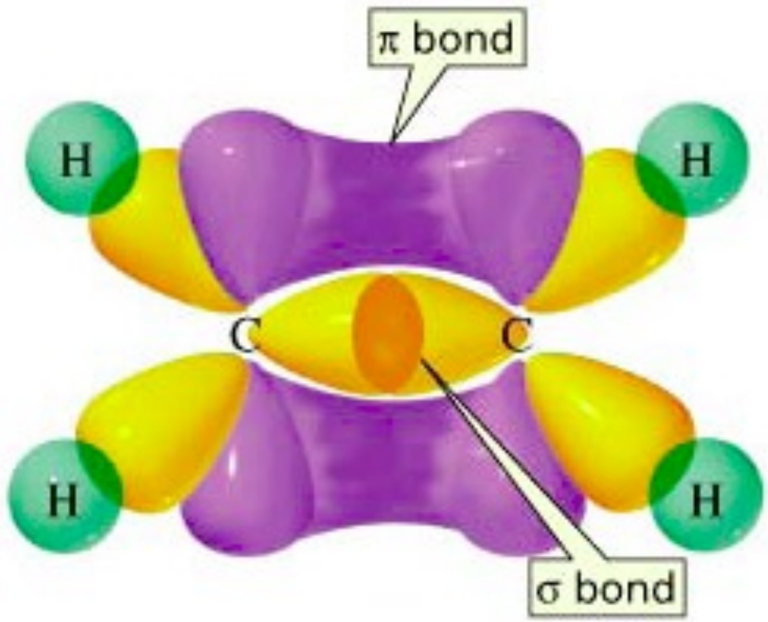
1-butene
(C_4H_8).

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 stonger than a single one (145 *vs* 83 kcal/mole) and shorter (1,34 *vs* 1,53 Å).

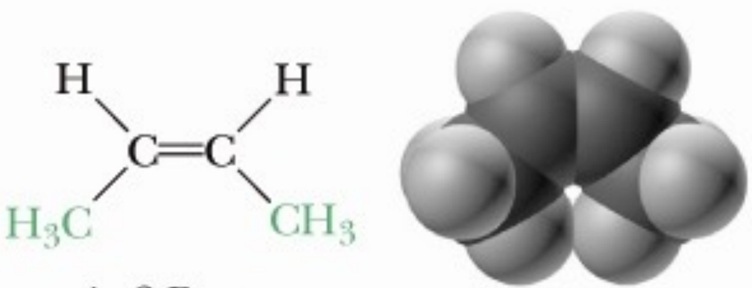
The molecule is planar



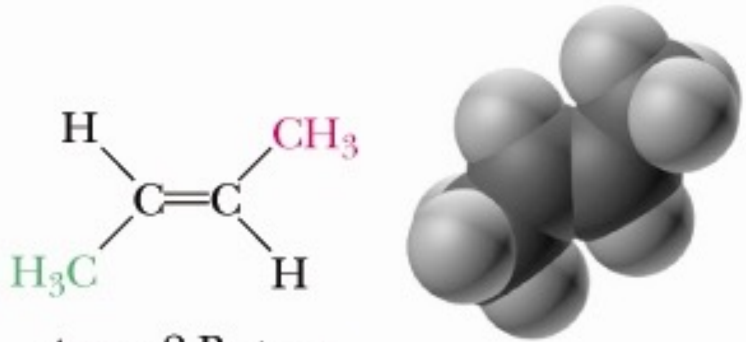


Geometric isomerism

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

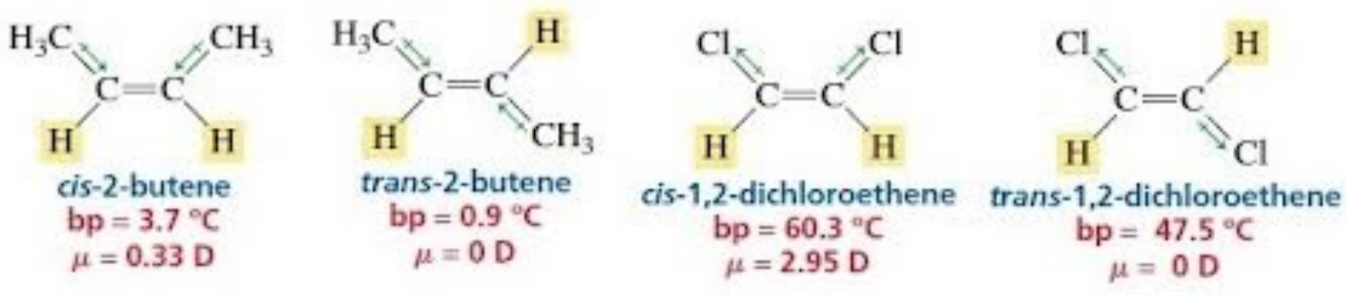


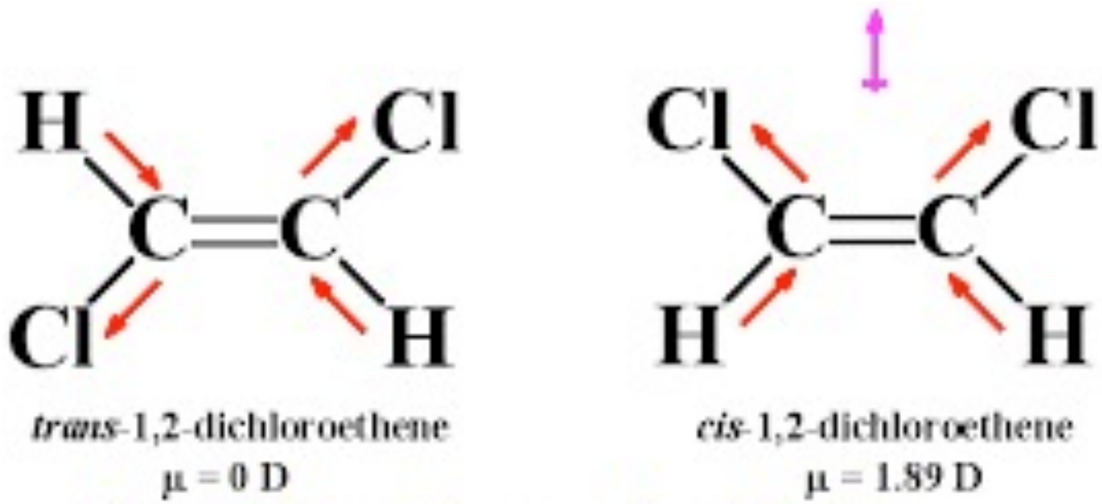
cis-2-Butene
pf – 139°C, pc 4°C



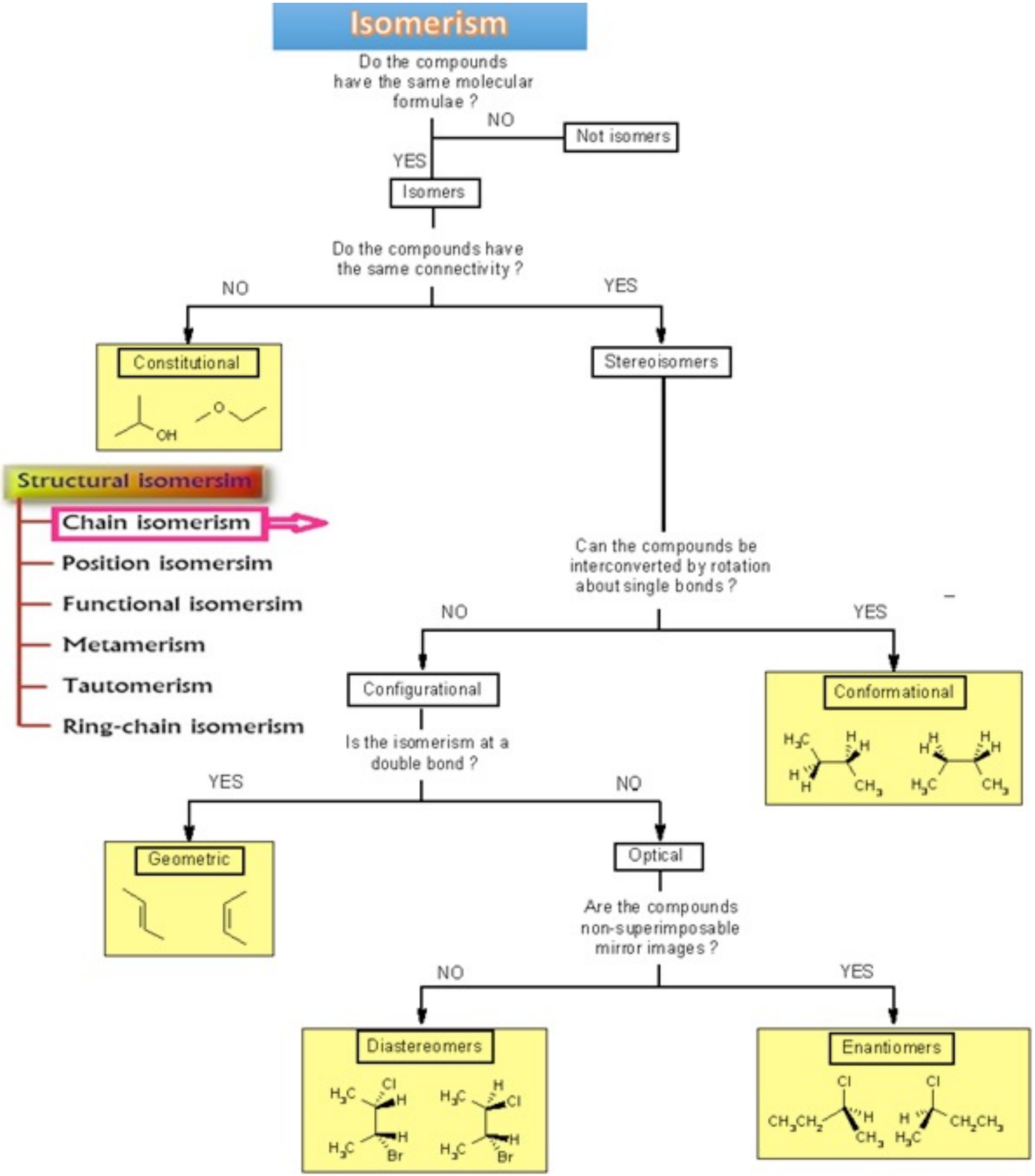
trans-2-Butene
pf – 106°C, pc 1°C

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.





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
Constitutional
OH
O
Stereoisomers
Structural isomersim
Chain isomerism
Position isomersim
Functional isomersim
Metamerism
Tautomerism
Ring-chain isomerism
Can the compounds be interconverted by rotation about single bonds ?
NO
YES
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Are the compounds non-superimposable mirror images ?
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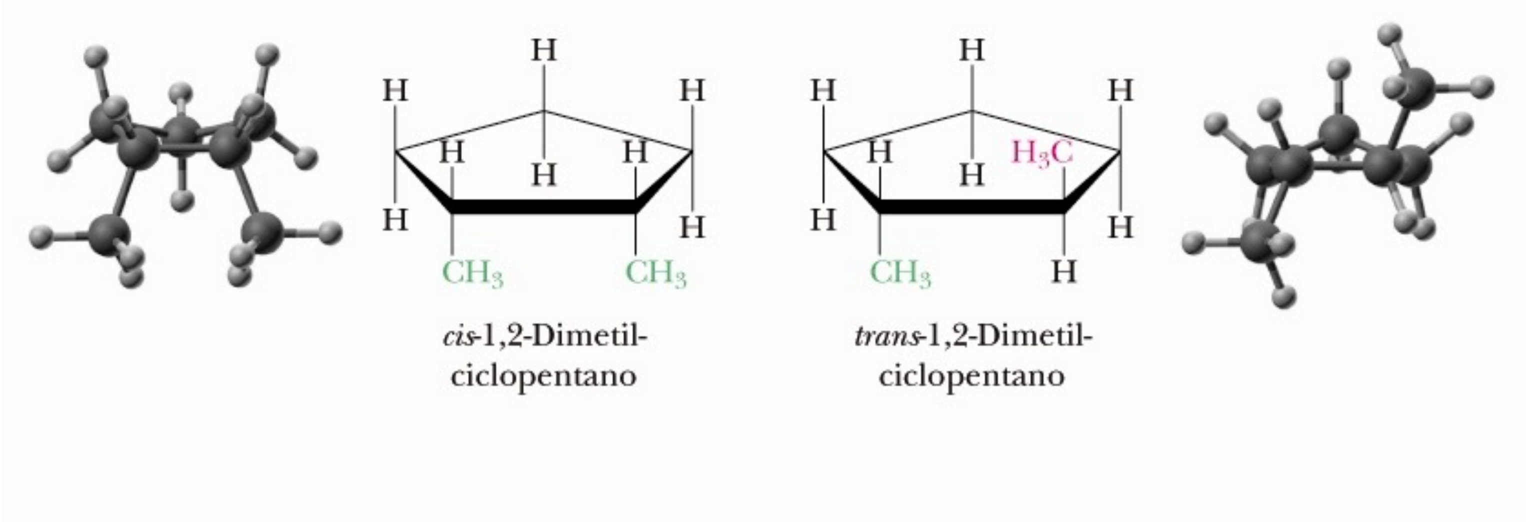
Enantiomers



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