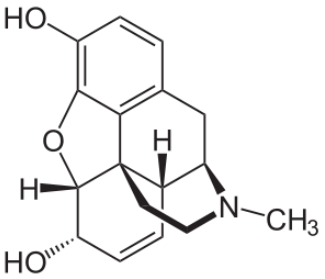
QFL0341 - Estrutura e Propriedades de Compostos Orgânicos - Noturno (agosto/06/2019)

Ligações químicas e grupos funcionais.

Nomenclatura e representação de moléculas orgânicas.

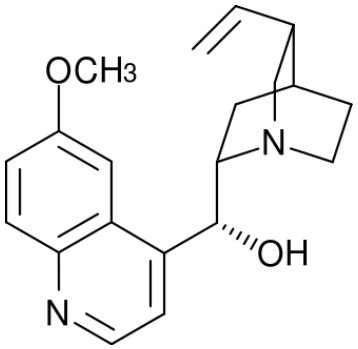
Hidrocarbonetos (alcanos, alcenos e acetilenos)

Structures of organic compounds such as natural products as mostly based on carbon-carbon bonding

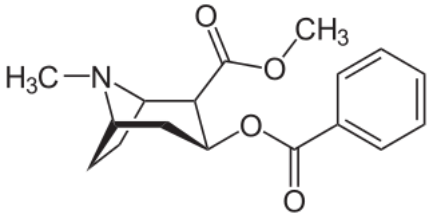


Morfina: Sertürner, 1805

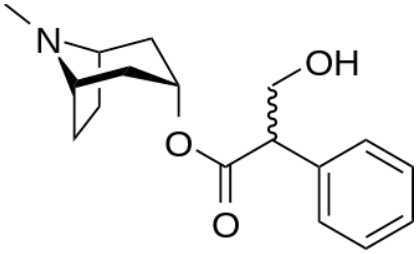
Papaver somniferum



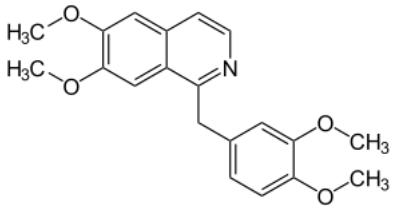
Quinina: Pelletier e Magendie, 1820



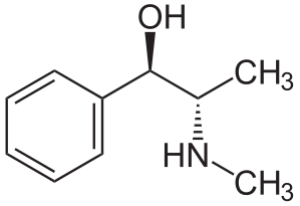
Cocaína: Wöhler, 1859.



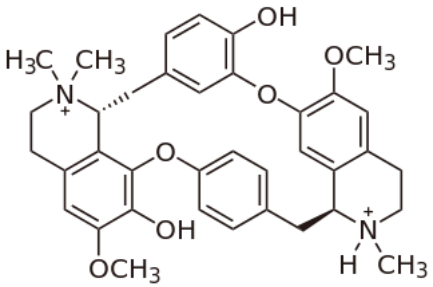
Atropina: Mein, 1831.



Papaverina: Merck, 1848.

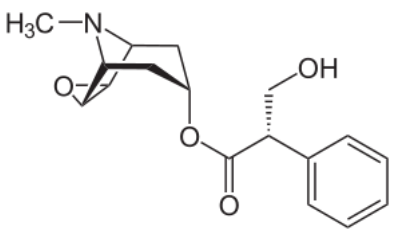


Efedrina: Nagai, 1885.



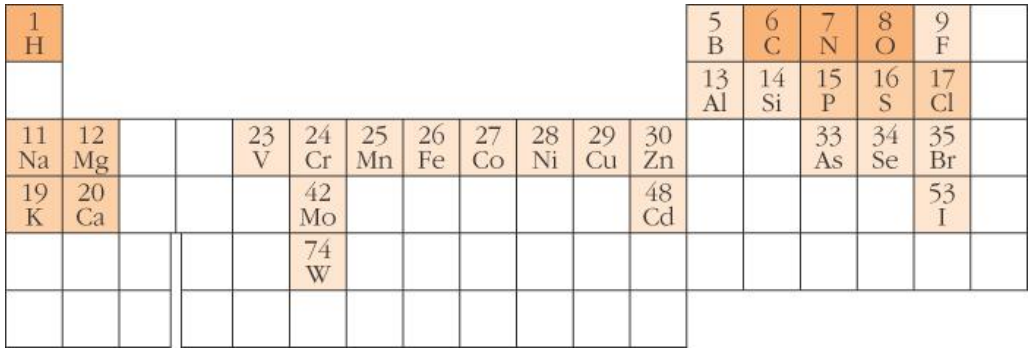
Tubocurarina: Boehm, 1895.

Chondrodendron tomentosum,



Escopolamina: Landenburg, 1881.

Organic chemistry: Elements of Life and their Availability



Element	Composition in Human beings (%)	Seawater (%)	Earth's crust (%)
Hydrogen	63	66	0.22
Oxygen	25.5	33	47
Carbon	9.5	0.0014	0.19
Nitrogen	1.4	<0.1	<0.1
Calcium	0.31	0.006	3.5
Phosphorus	0.22	<0.1	<0.1
Chloride	0.03	0.33	<0.1
Potassium	0.06	0.006	2.5
Sulfur	0.05	0.017	<0.1
Sodium	0.03	0.28	2.5
Magnesium	0.01	0.003	2.2
Silicon	<0.1	<0.1	28
Aluminum	<0.1	<0.1	7.9
Iron	<0.1	<0.1	4.5
Titanium	<0.1	<0.1	0.46
All others	<0.1	<0.1	<0.1

Por que a vida é baseada em compostos orgânicos a base de carbono?

Dissociation energy of some chemical bond

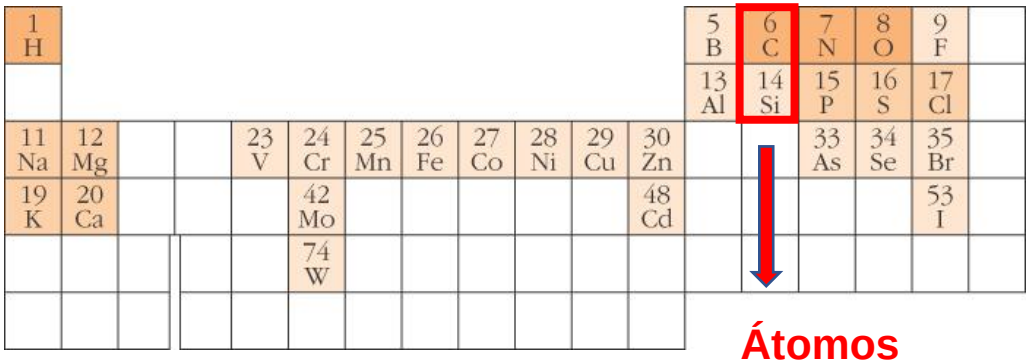
Bond	DH° kcal/mol	DH° kJ/mol
$CH_3—H$	105	439
$CH_3CH_2—H$	101	423
$CH_3CH_2CH_2—H$	101	423
$(CH_3)_2CH—H$	99	414
$(CH_3)_3C—H$	97	406
$CH_3—CH_3$	88	368
$CH_3CH_2—CH_3$	85	355
$(CH_3)_2CH—CH_3$	84	351
$(CH_3)_3C—CH_3$	80	334
$H_2C=CH_2$	152	635
$HC\equiv CH$	200	836

Bond	DH° kcal/mol	DH° kJ/mol
$H—H$	104	435
$F—F$	38	159
$Cl—Cl$	58	242
$Br—Br$	46	192
$I—I$	36	150
$H—F$	138	568
$H—Cl$	103	431
$H—Br$	88	366
$H—I$	71	297
$CH_3—F$	108	451
$CH_3—Cl$	84	349
$CH_3CH_2—Cl$	82	343
$(CH_3)_2CH—Cl$	81	338
$(CH_3)_3C—Cl$	79	330
$CH_3—Br$	70	293
$CH_3CH_2—Br$	69	289
$(CH_3)_2CH—Br$	68	285
$(CH_3)_3C—Br$	63	264
$CH_3—I$	56	234
$CH_3CH_2—I$	55	230

C≡O	1080 kJ/mol
N≡N	946
C≡N	891

PhCOO-OCOPh (30kcal/mol)

Por que a vida não poderia ser baseada em compostos de silicio?



Átomos tetravalentes

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Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure element in the Earth's crust.

It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates.

The Si–C bond can be broken more readily than typical C–C bonds.

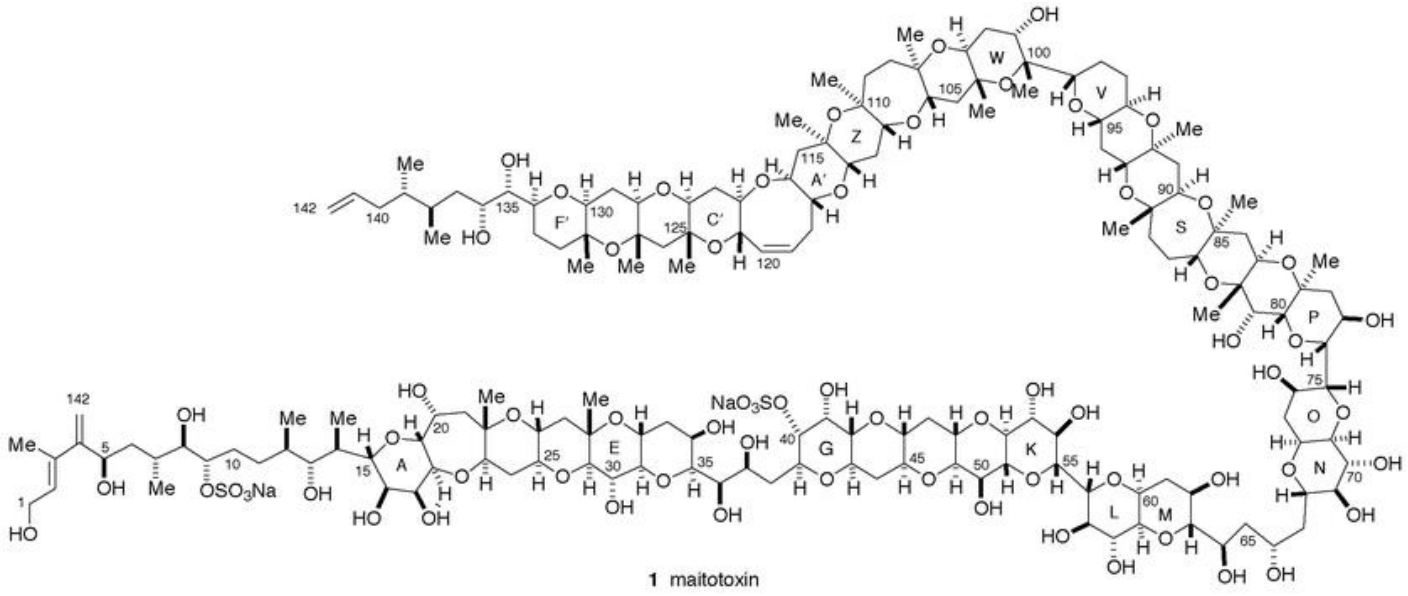
Lenght of bonds		dissociation energy
C – **Si**	1.86 A^{o}	451 kJ/mol
C – C	1.54 A^{o}	607 kJ/mol

The C–Si bond is polarised towards carbon due to carbon's greater electronegativity (C 2.55 vs Si 1.80).

CO_2 is a gas

SiO_2 is a solid (such as sand)

Complex organic molecule



1 maitotoxin

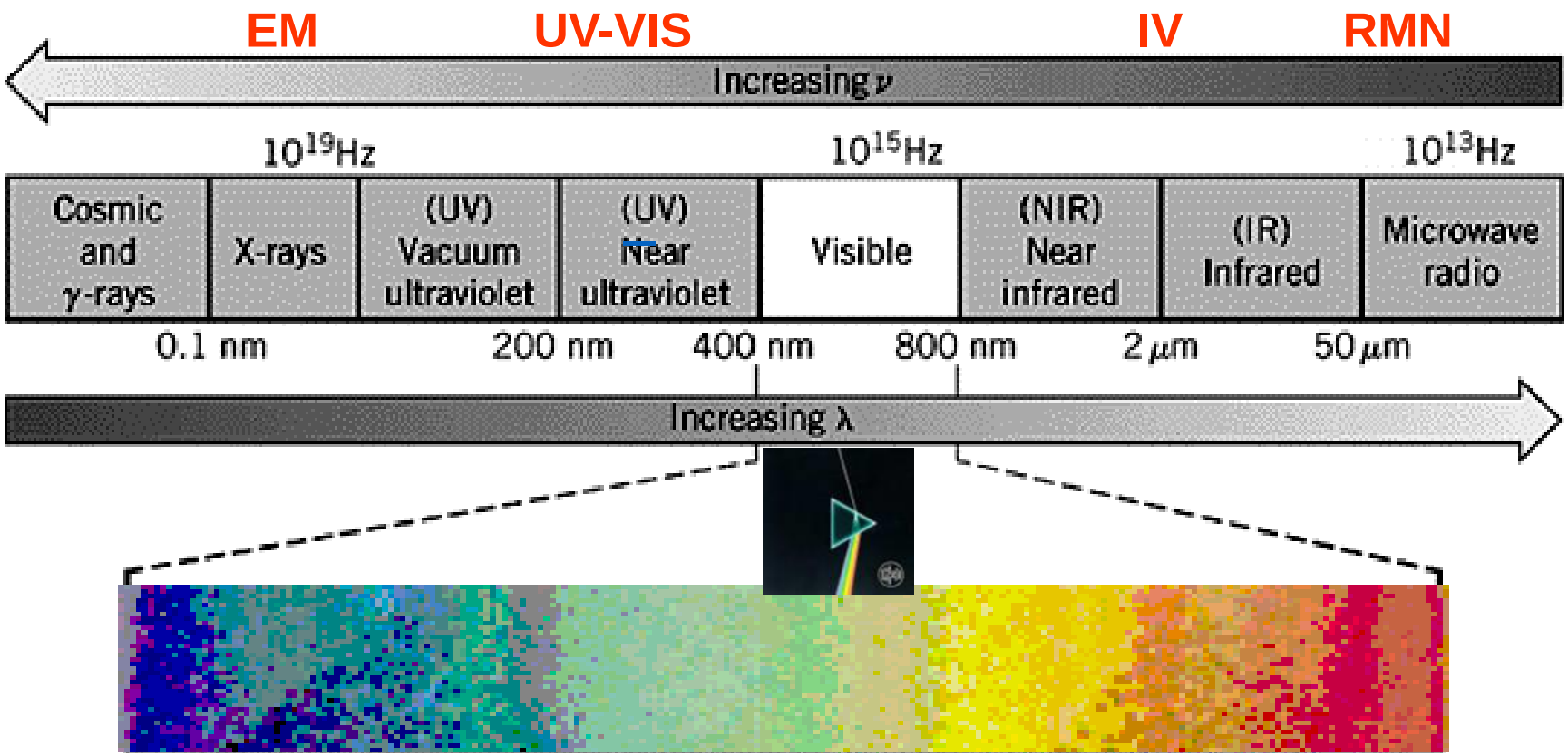
Selected physicochemical properties of **1** are as follows;
a white amorphous solid, $[\alpha]_D^{25}$ +16.8 (*c* 0.36, MeOH-H_2O, 1:1);

Bond breaking

Vibrational/rotational excitation

Eletronic transitions

Nuclear spin transitions



Formation of organic molecules (simulation of primitive atmosphere)

Miller´s experiment

CH_4, N_2, H_2O, NH_3

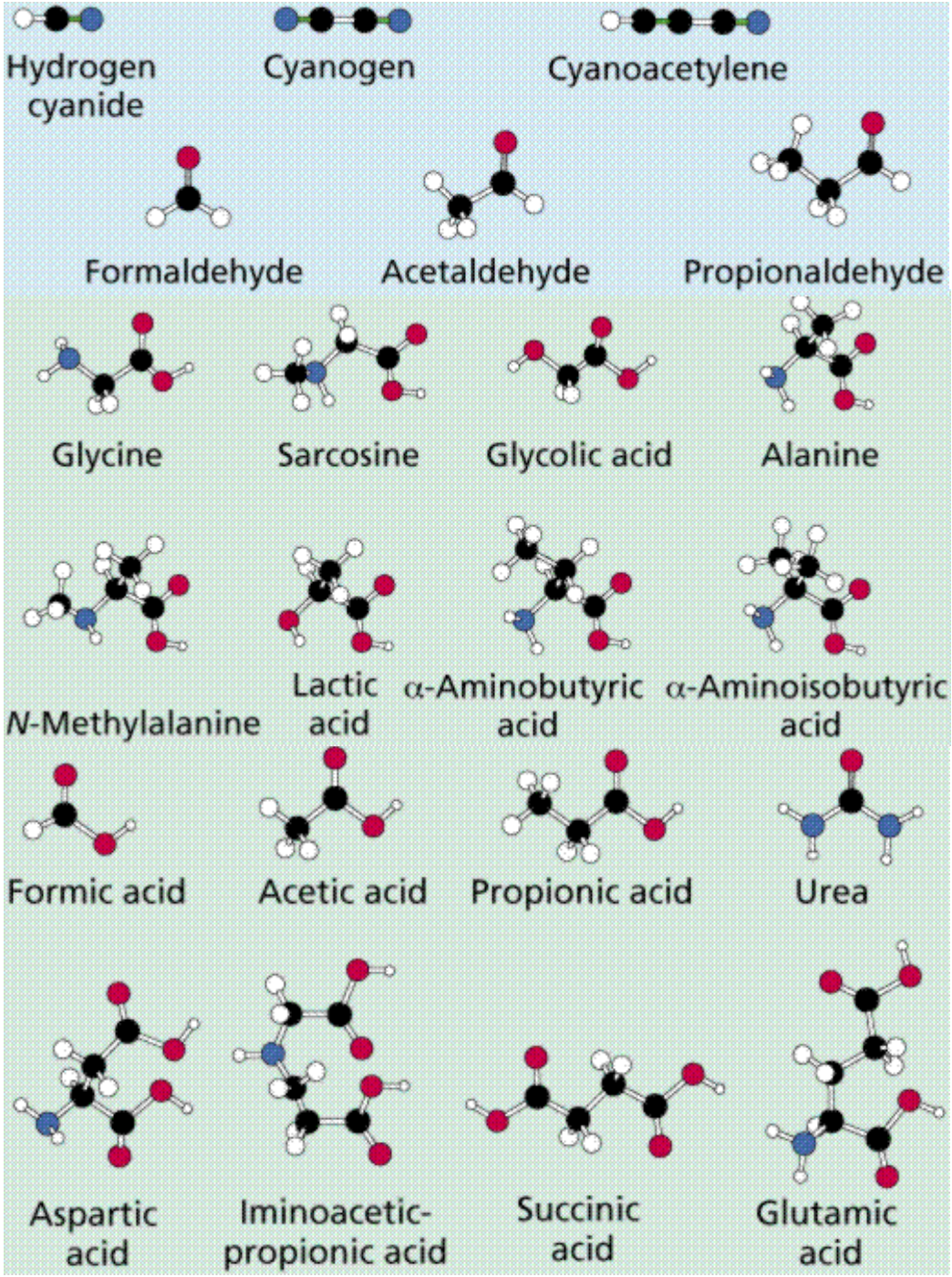
⇩

Electrical Discharge (causing radicalar reactions)

Complex molecules Aminoacids and other biomolecules

Miller, S. L., Urey, H. C., 1959. Organic compound synthesis on the primitive earth. *Science* 130, 245-251.

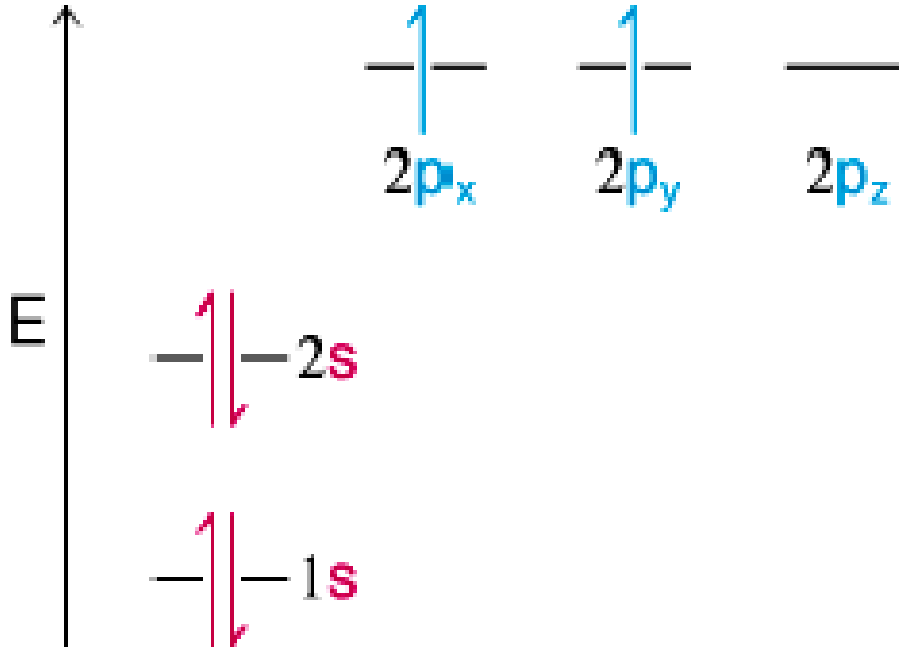
Organic compounds produced in Miller's experiment



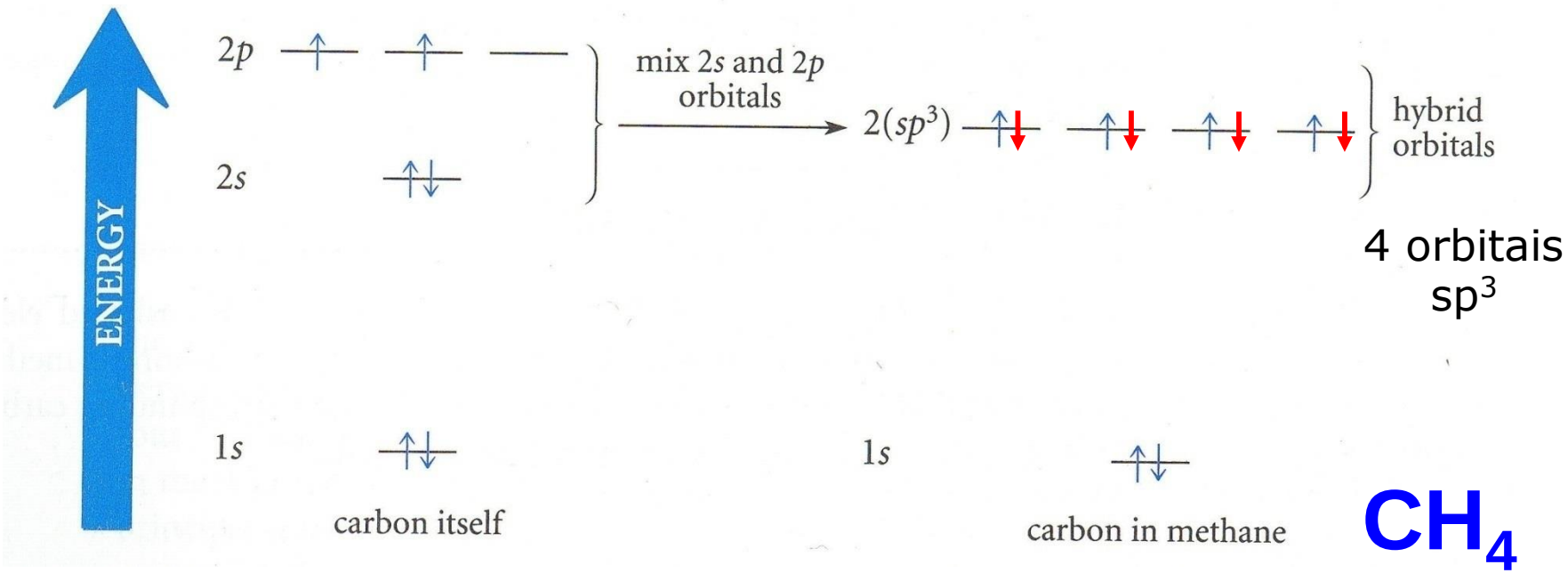
Science 1953; **117**: 528-529.

Átomo de carbono no estado fundamental:

(número atômico=6): $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$



Formação de orbitais híbridos sp^3 para o átomo de carbono



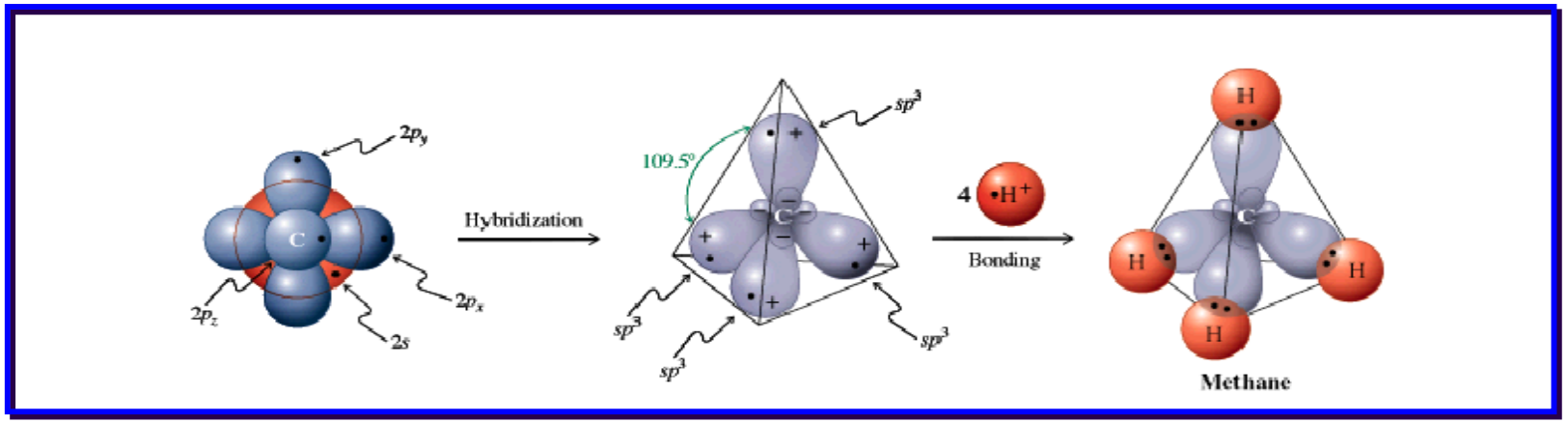
4 orbitais sp^3

CH_4

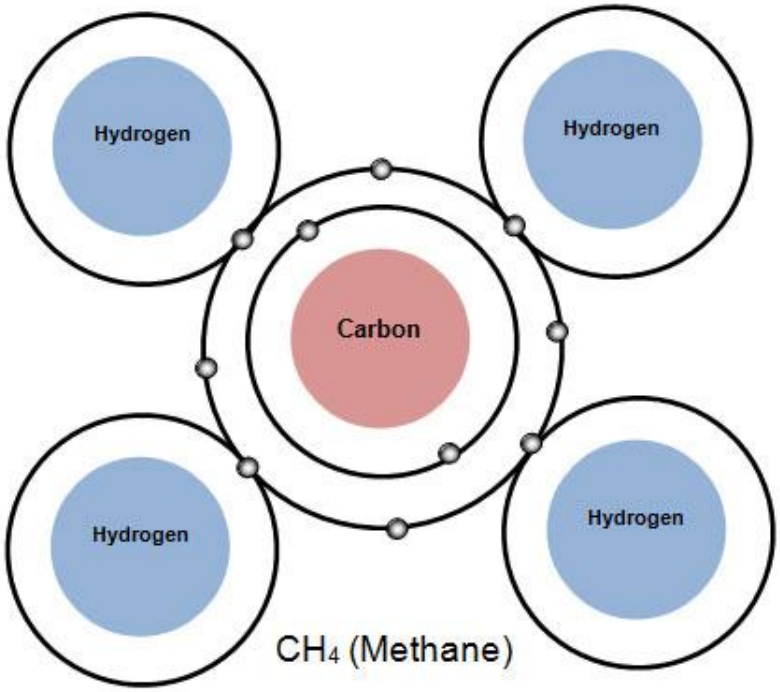
C (nº atômico: 6):

$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$

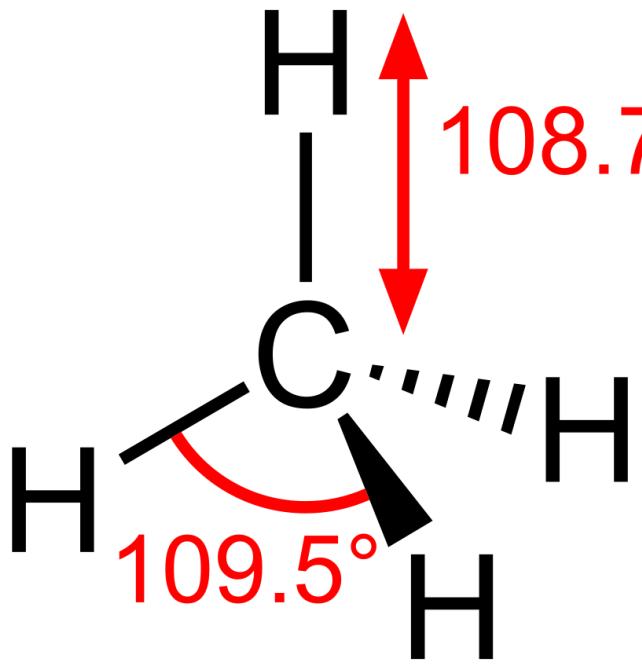
Por que tetraédrico???



Methane



Structure of Methane



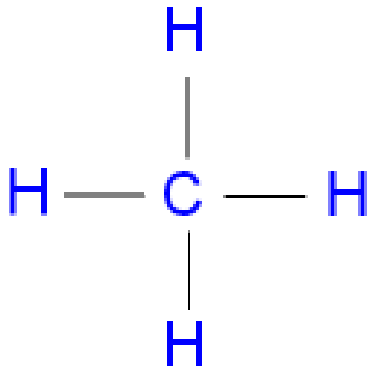
Methane

3D Jsmol

https://www.worldofmolecules.com/

https://www.worldofmolecules.com/3D/methane_3d.htm

Methane **CH_4**

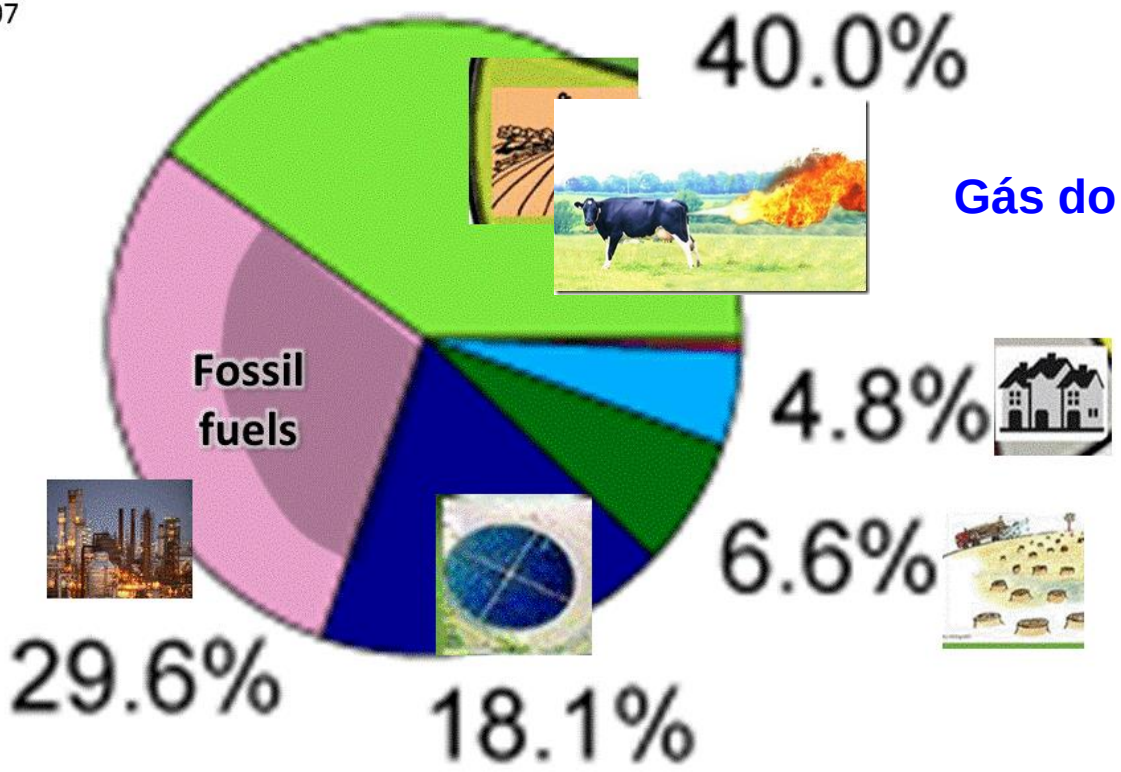


Greek "*methy*“ (alcohol from wood)

Chemical formula	CH_4
Molar mass	16.04 g·mol^{-1}
Appearance	Colorless gas
Odor	Odorless
Density	•0.657 g·L^{-1} (gas, 25 °C, 1 atm) •0.717 g·L^{-1} (gas, 0 °C, 1 atm) •422.62 g·L^{-1} (liquid, −162 °C)
Melting point	−182.5 °C;
Boiling point	−161.50 °C;
Solubility in water	22.7 mg·L^{-1}
Solubility	Soluble in ethanol, diethyl ether, benzene, toluene, methanol, acetone

Global methane emissions 18% of total

IPCC 2007

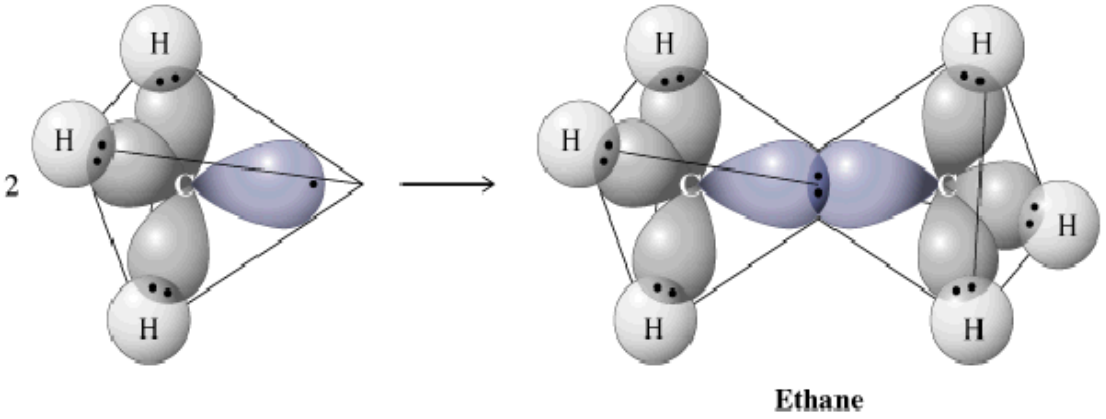


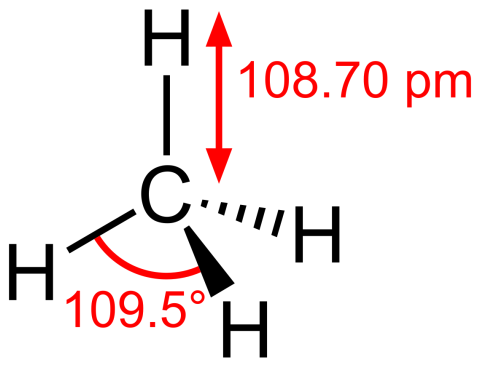
Gás do pum!

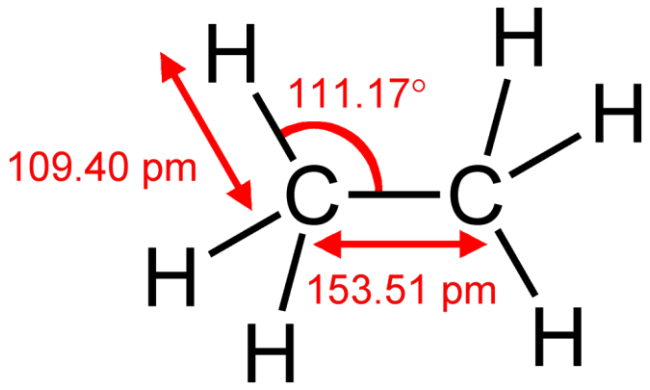
Etano

- ✓ Uma ligação sigma (σ) é uma ligação covalente em que a sobreposição dos orbitais de uma ligação ocorre ao longo do eixo dos dois núcleos.
- ✓ De modo geral, os esqueletos das moléculas orgânicas são formados de átomos unidos por ligações sigma.

$H_3C\cdot + \cdot CH_3$



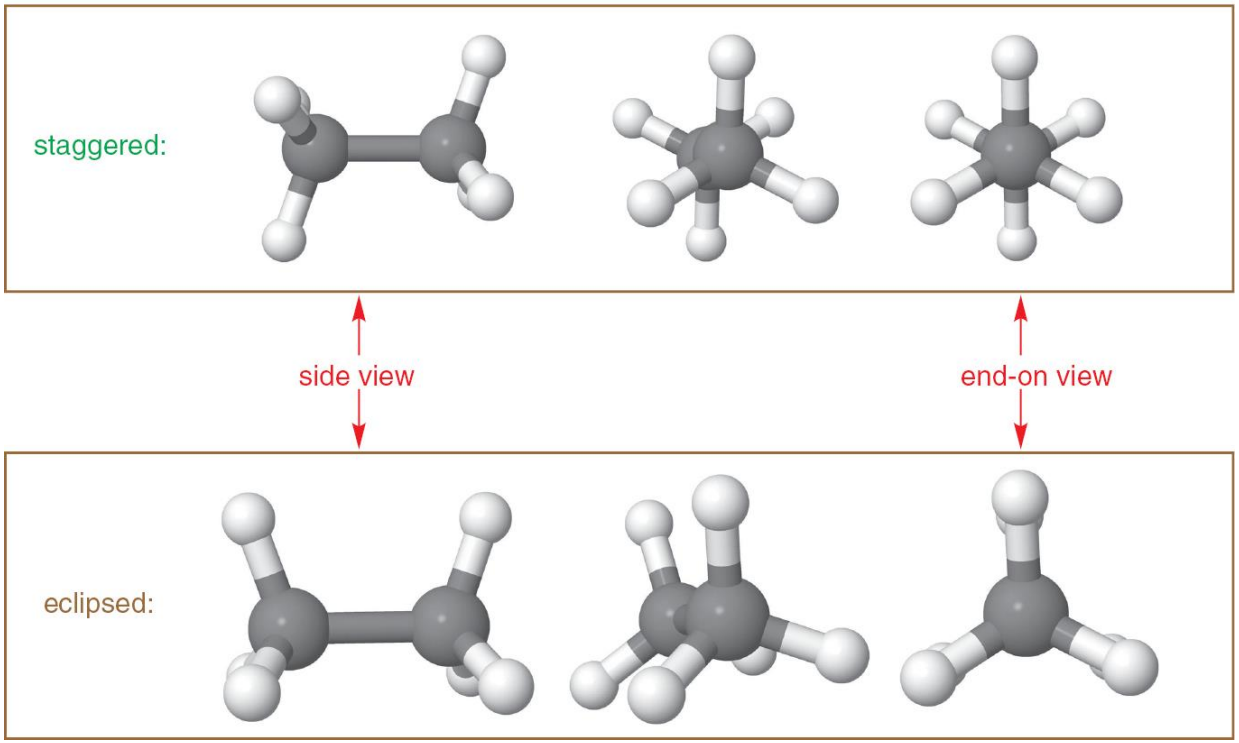


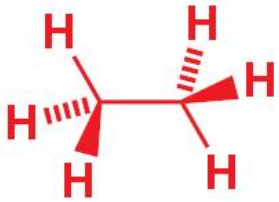


Conformações na molécula do etano

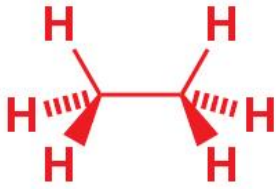
https://pubchem.ncbi.nlm.nih.gov/compound/Ethane#section=3D-Conformer

Confôrmero escalonado (staggered)





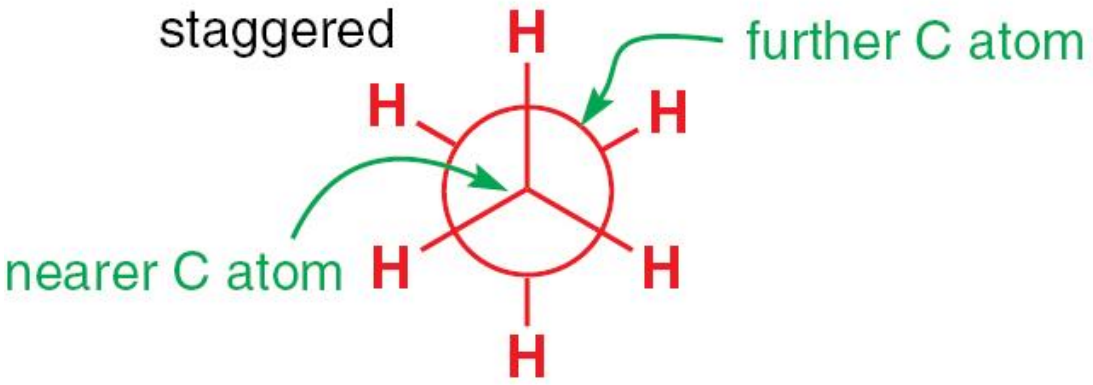
the staggered conformation of ethane

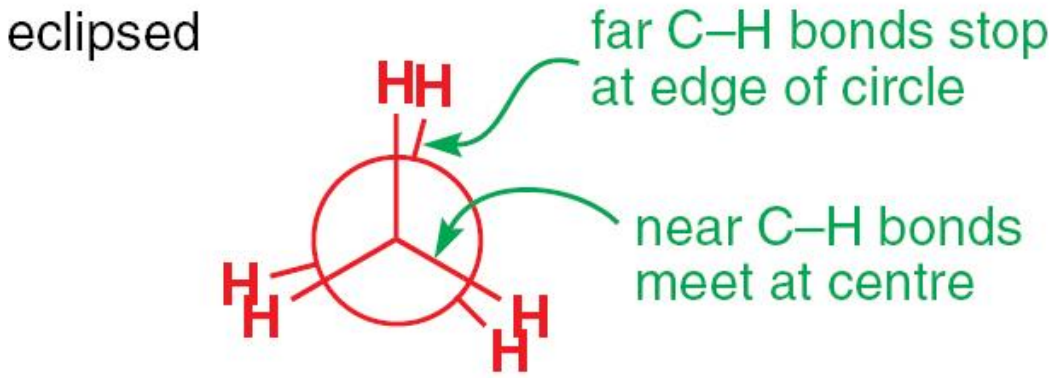


the eclipsed conformation of ethane

Confôrmero eclipsado

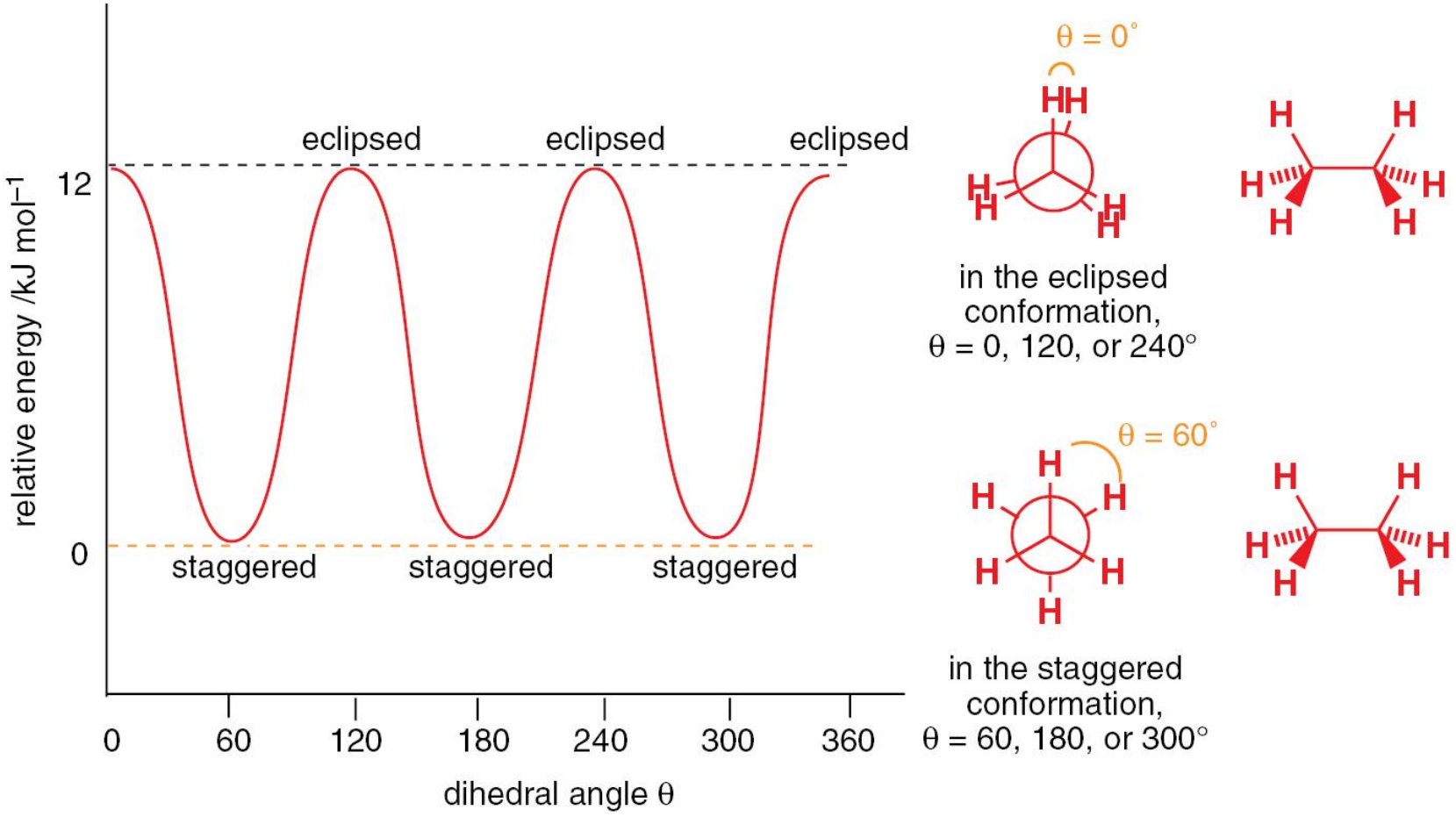
Conformações na molécula do etano





Qual confôrmero é mais estável?

Barreiras rotacionais para o etano

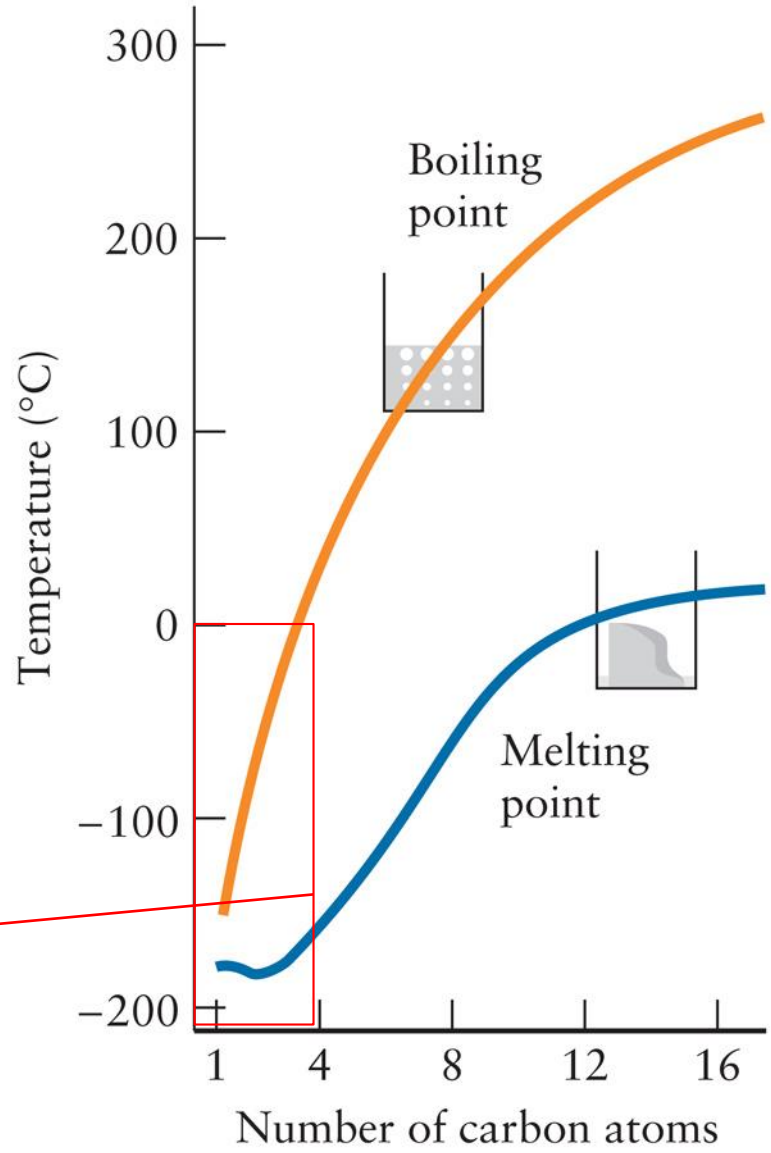


Properties of Alkanes

Hydrocarbons are nonpolar

- The only intermolecular force between adjacent hydrocarbons is the London Force

Methane through Butane
are gases at room temperature



Crude Oil Refining

Distillate Fraction	Boiling Point (°C)	Carbon Atoms per Molecule
Gases	below 30	1-4
Gasoline	30-210	5-12
Naphtha	100-200	8-12
Kerosene & Jet Fuel	150-250	11-13
Diesel & Fuel Oil	160-400	13-17
Atmospheric Gas Oil	220-345	
Heavy Fuel Oil	315-540	20-45
Atmospheric Residue	over 450	over 30
Vacuum Residue	over 615	over 60

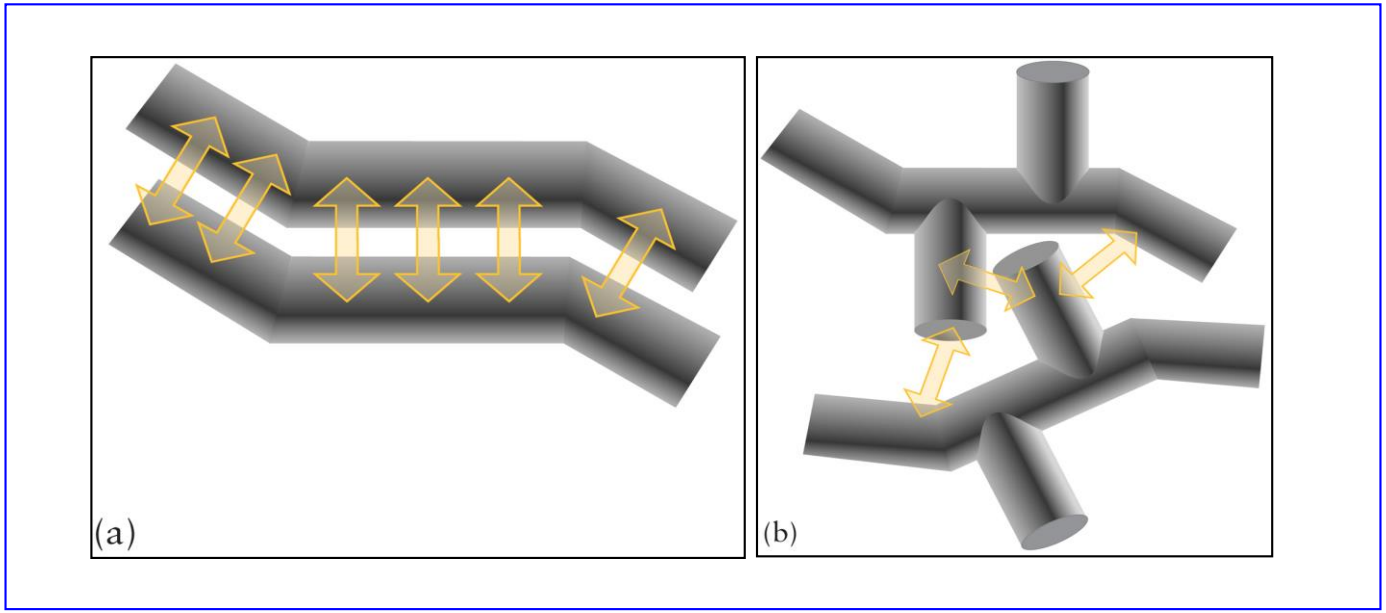
Propriedades Físicas

- Isômeros constitucionais têm propriedades físicas diferentes.

C_6H_{14}

Nome	PF (°C)	PE (°C)	Densidade (g/mL)
hexano	-95	68,7	0,659
2-metilpentano	-154	60,3	0,653
3-metilpentano	-118	63,3	0,664
2,3-dimetilbutano	-129	58,0	0,661
2,2-dimetilbutano	-98	49,7	0,649

Properties of Alkanes



•Long chain hydrocarbons have higher melting points than branched chains with the same number of carbons

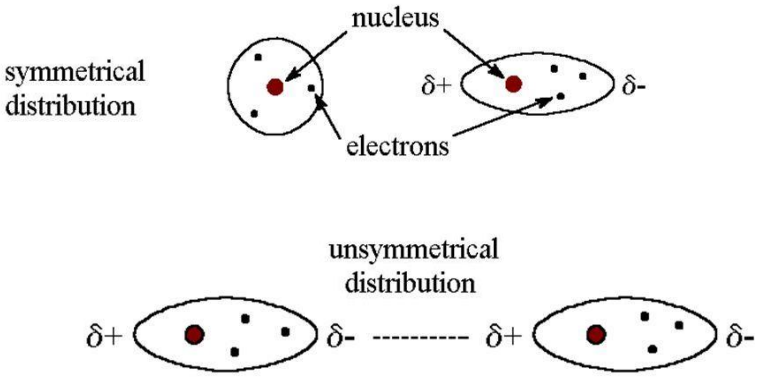
•Fatty acids in cell membranes take advantage of this to make themselves more fluid.

Boiling properties of alkanes

TABLE | 4.4 STRUCTURE, NAME, AND PROPERTIES OF SELECTED HYDROCARBONS

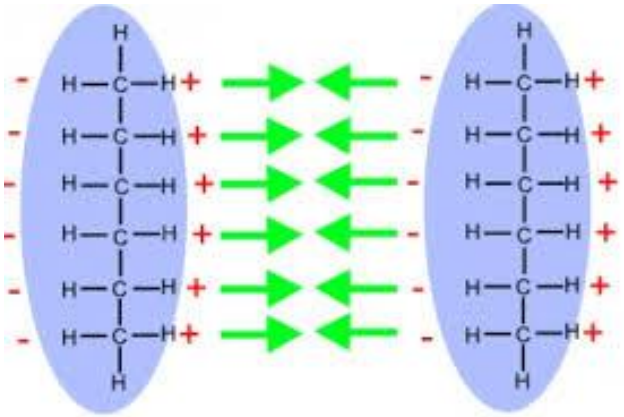
Structural Formula	IUPAC Name	Common Name	Boiling Point (°C)
Alkanes			
CH_4	Methane		−164
CH_3CH_3	Ethane		−89
$CH_3CH_2CH_3$	Propane		−42
$CH_3CH_2CH_2CH_3$	Butane		0
$CH_3CH_2CH_2CH_2CH_3$	Pentane		36

London Dispersion Forces



Temporary dipoles caused by the movement of electrons in a molecule.

German-American physicist Fritz London.



(**LDF**, also known as dispersion forces, London forces, instantaneous dipole–induced dipole forces, or loosely van der Waals forces)

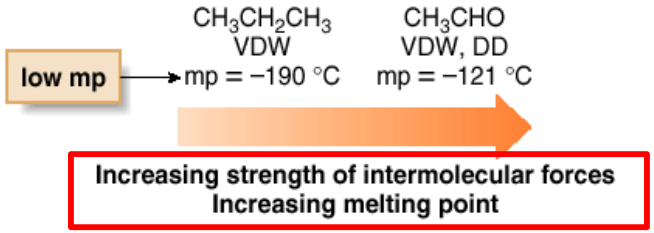
Physical Properties of Some Organic Compounds

Formula	IUPAC Name	Molecular Weight	Boiling Point	Water Solubility
$CH_3(CH_2)_2CO_2H$	butanoic acid	88	164 °C	very soluble
$CH_3(CH_2)_4OH$	1-pentanol	88	138 °C	slightly soluble
$CH_3(CH_2)_3CHO$	pentanal	86	103 °C	slightly soluble
$CH_3CO_2C_2H_5$	ethyl ethanoate	88	77 °C	moderately soluble
$CH_3CH_2CO_2CH_3$	methyl propanoate	88	80 °C	slightly soluble
$CH_3(CH_2)_2CONH_2$	butanamide	87	216 °C	soluble
$CH_3CON(CH_3)_2$	*N*,*N*-dimethylethanamide	87	165 °C	very soluble
$CH_3(CH_2)_4NH_2$	1-aminobutane	87	103 °C	very soluble
$CH_3(CH_2)_3CN$	pentanenitrile	83	140 °C	slightly soluble
$CH_3(CH_2)_4CH_3$	hexane	86	69 °C	insoluble

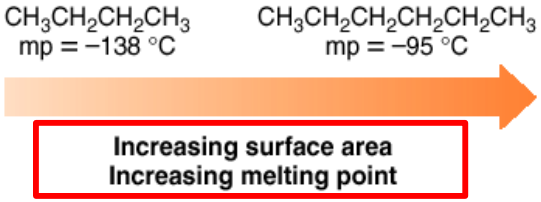
What is causing such behavior in boiling points?

Some general trends about physical properties of alkanes

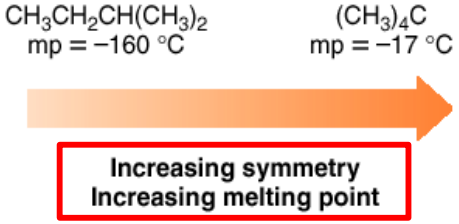
Property	Observation
Melting point	• Alkanes have low mp's compared to more polar compounds of comparable size.



• Mp increases as the number of carbons increases because of increased surface area.



• Mp increases with increased symmetry.



Solubility	• Alkanes are soluble in organic solvents. • Alkanes are insoluble in water.

Key: bp = boiling point; mp = melting point; VDW = van der Waals; DD = dipole–dipole; HB = hydrogen bonding; MW = molecular weight

Chemical properties of Alkanes

- Parafins are what alkanes were once called and you'll sometimes hear the term used today
  - Means "*Little Affinity*"

- They got this name because they do not react with:
  Strong Acids
  Strong Bases
  Oxidizing Agents

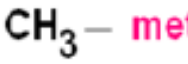
- Why?
  - The bond enthalpies of the C-C and C-H bonds are so high

- Alkanes will undergo 2 types of reactions:
  1. Combustion
  2. Substitution: Some atom (say a halide) replaces a hydrogen on the hydrocarbon (by radicalar reactions)

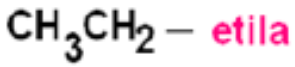
Nomenclatura para hidrocarbonetos alifáticos e saturados

Number of C atoms	Molecular formula	Name (*n*-alkane)	Number of constitutional isomers
1	CH_4	methane	—
2	C_2H_6	ethane	—
3	C_3H_8	propane	—
4	C_4H_{10}	butane	2
5	C_5H_{12}	pentane	3
6	C_6H_{14}	hexane	5
7	C_7H_{16}	heptane	9
8	C_8H_{18}	octane	18
9	C_9H_{20}	nonane	35
10	$C_{10}H_{22}$	decane	75
20	$C_{20}H_{42}$	eicosane	366,319

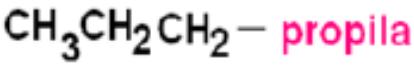
Nomes de substituíntes alquílicos (quando parte de uma molécula maior)



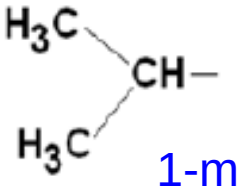
metila (Me)



etila (Et)

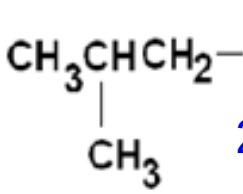


propila (Pr)



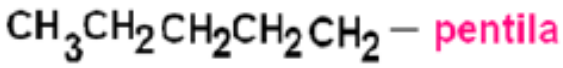
iso-propila (i-Pr)

1-metiletil-



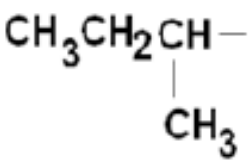
iso-butila (i-Bu)

2-metilpropil-

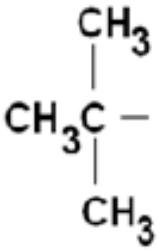


pentila (pent)

1-metilpropil-

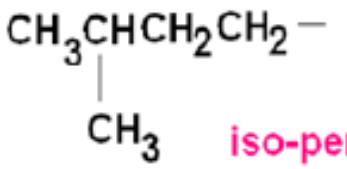


sec-butila (sec-Bu)



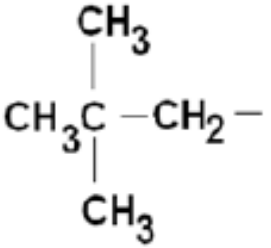
terc-butila (t-Bu)

1,1-dimetiletil-



iso-pentila

(i-pent)



neo-pentila

(neo-pent)

Regras para nomear compostos orgânicos

1) Determine a cadeia carbônica mais longa (vide problema 5 – lista 1);

2) Identifique (com nomes) os substituíntes ligados a cadeia;
(*não use o termo radical, que deve ser utilizada para espécie reativa*)

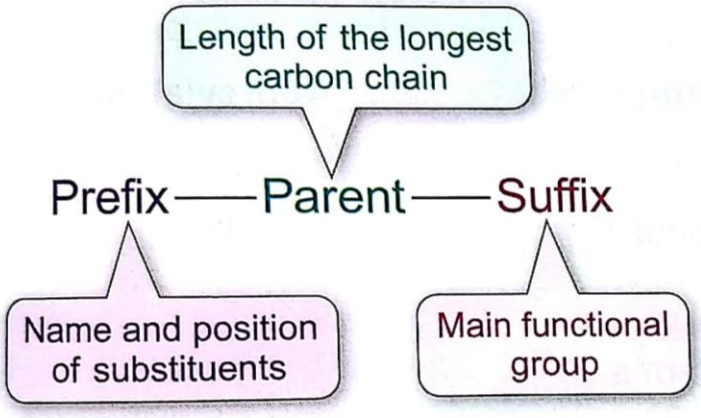
3) Numere a cadeia principal tendo a ramificação a menor numeração entre as demais;

4) Designe as posições dos substituíntes pelos números onde se encontram;

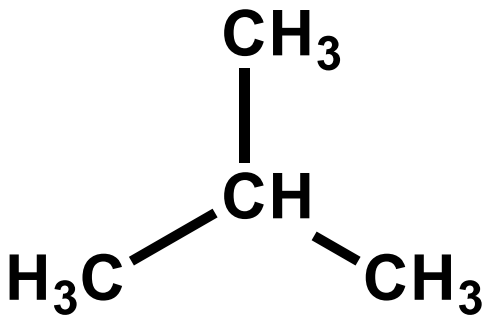
5) Escreva o nome complete da substância, listando os substituíntes em order alfabética;

Os prefixos *di-, tri-, tetra-, sec-* e *terc-* não são considerados na priorização;

Mas *iso-*, *ciclo-* e *neo-* devem ser considerados na ordem alfabética



Qual o nome IUPAC ?

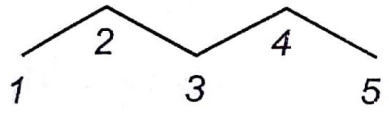


2-metil - prop - ano

Nome IUPAC:
2-metilpropano

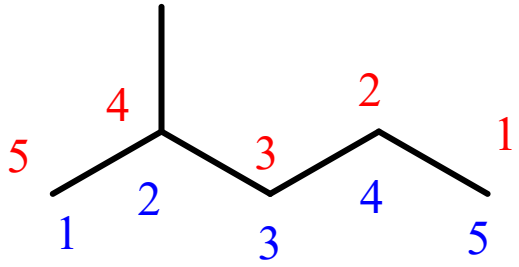
Nome comum:
isobutano

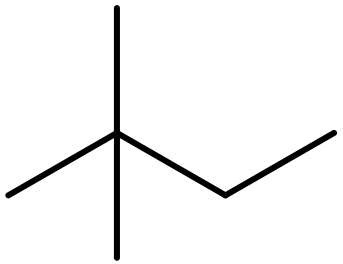
Qual a numeração correta?

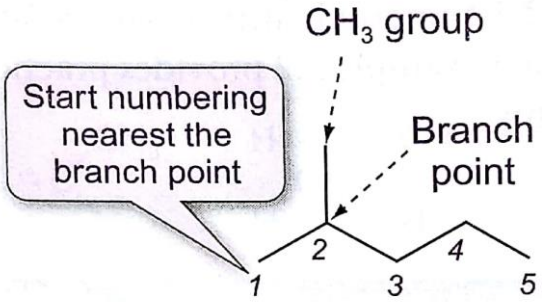


pentane

Five carbon chain with no substituents

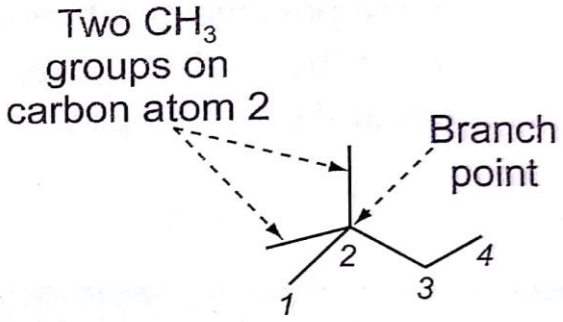






2-methylpentane

Five carbon chain with a methyl group on carbon atom 2



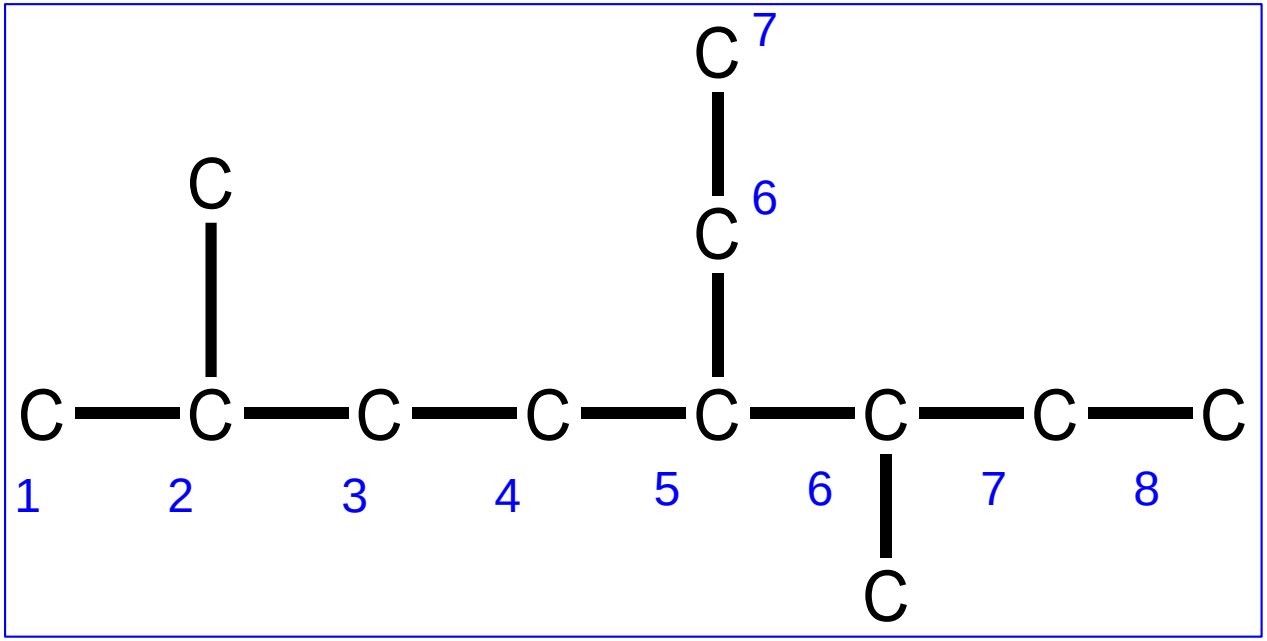
2,2-dimethylbutane

Four carbon chain with two methyl groups on carbon atom 2

Not 4-methylpentane!

Regras para definir a cadeira carbônica mais importante

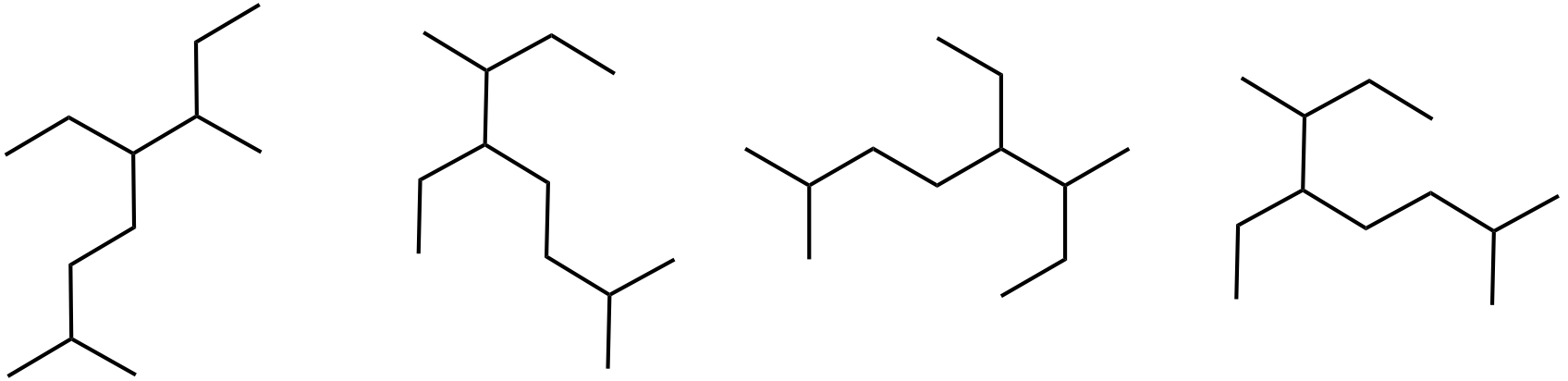
1. Encontre a cadeia mais longa e adicione o sufixo.

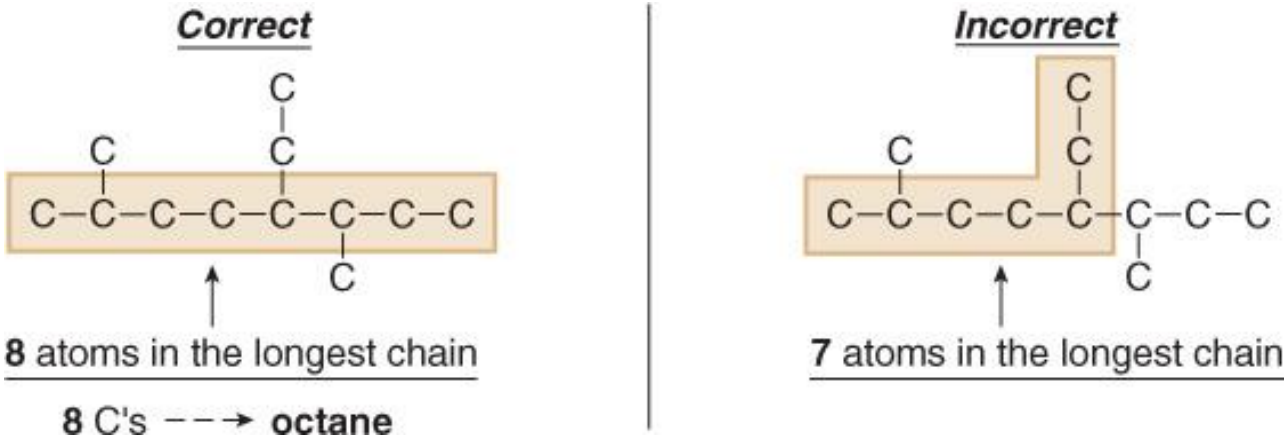


Regras para definir a cadeira carbônica mais importante

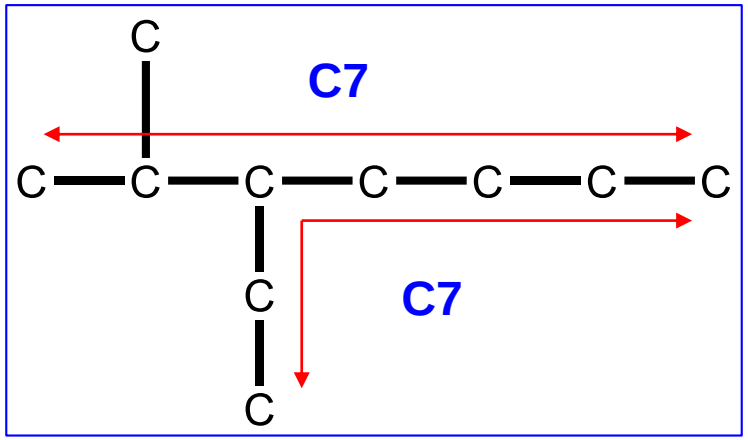
1. Encontre a cadeia mais longa e adicione o sufixo.

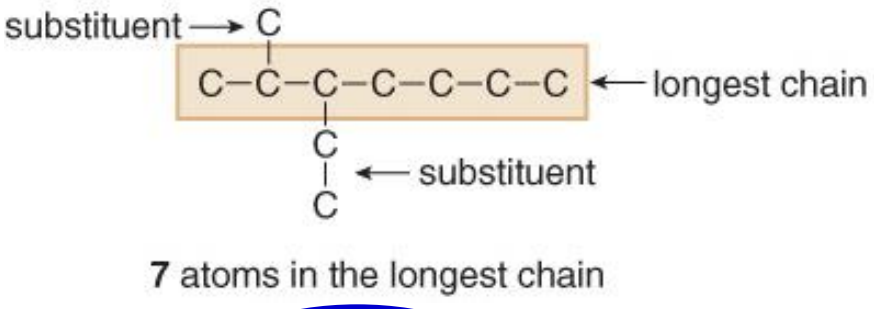
A molécula pode estar esticada, dobrada… não importa!

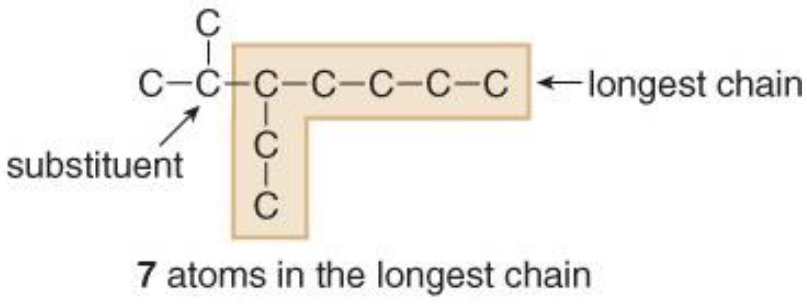


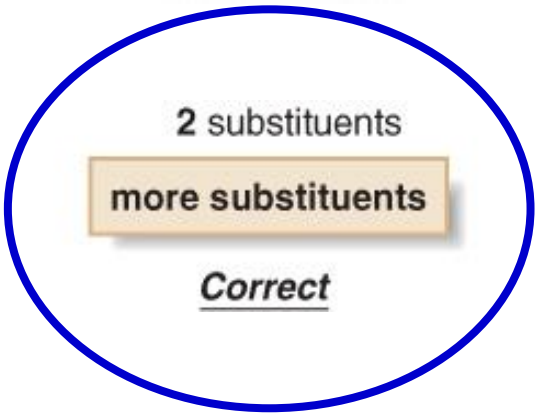


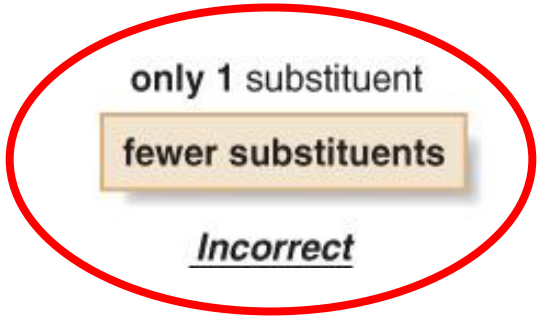
E quando há duas possibilidades de cadeia com mesmo comprimento?





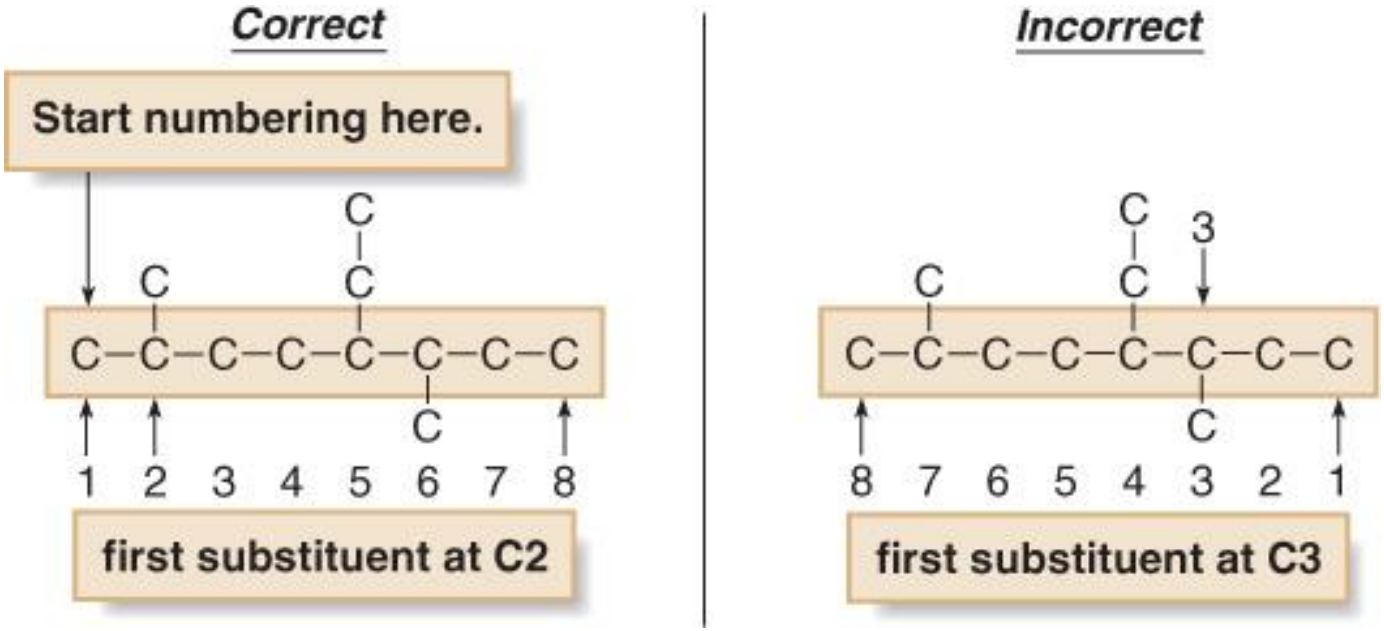






Quando há duas opções para a mesma cadeia

Escolha a cadeia no qual o *primeiro substituínte tenha a menor numeração*.

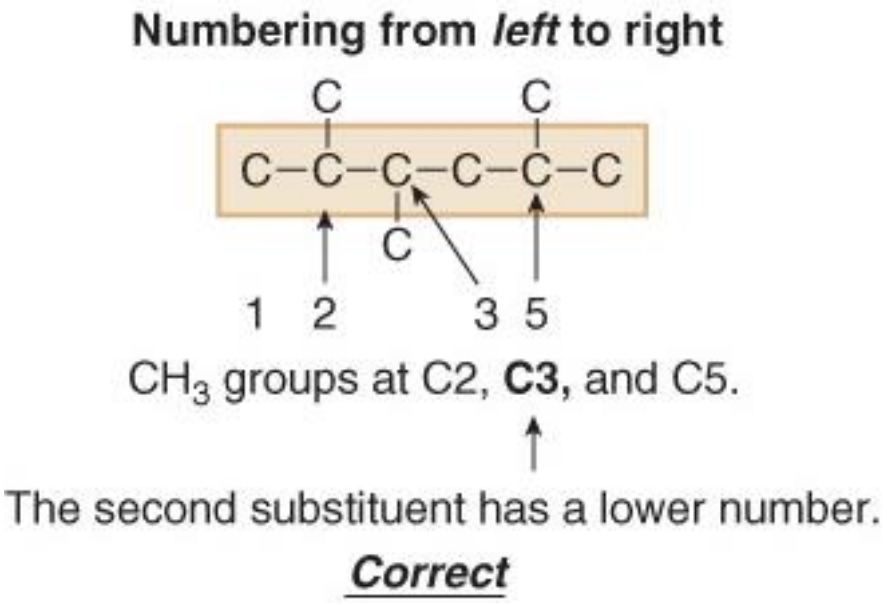


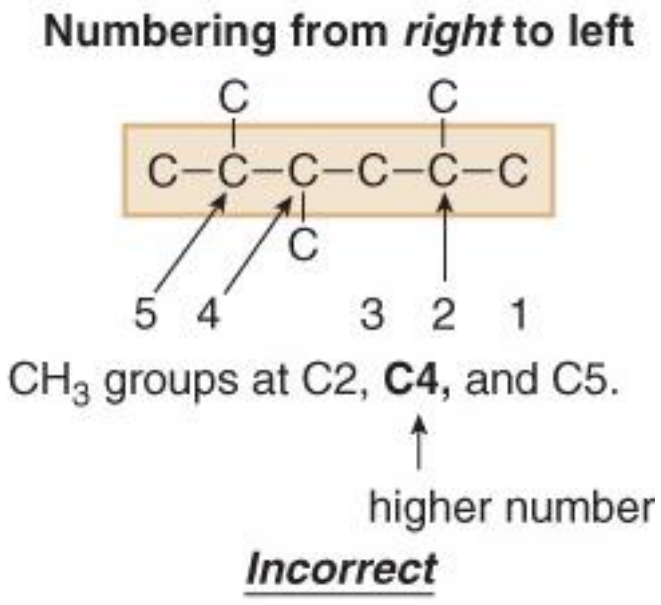
Primeiro substituinte em C-2

Primeiro substituinte em C-3 (errado)

E quando há duas opções para numerar o substituinte com o menor número (p. ex. em C2)

Nesse caso, o segundo substituinte deve ter o menor número.

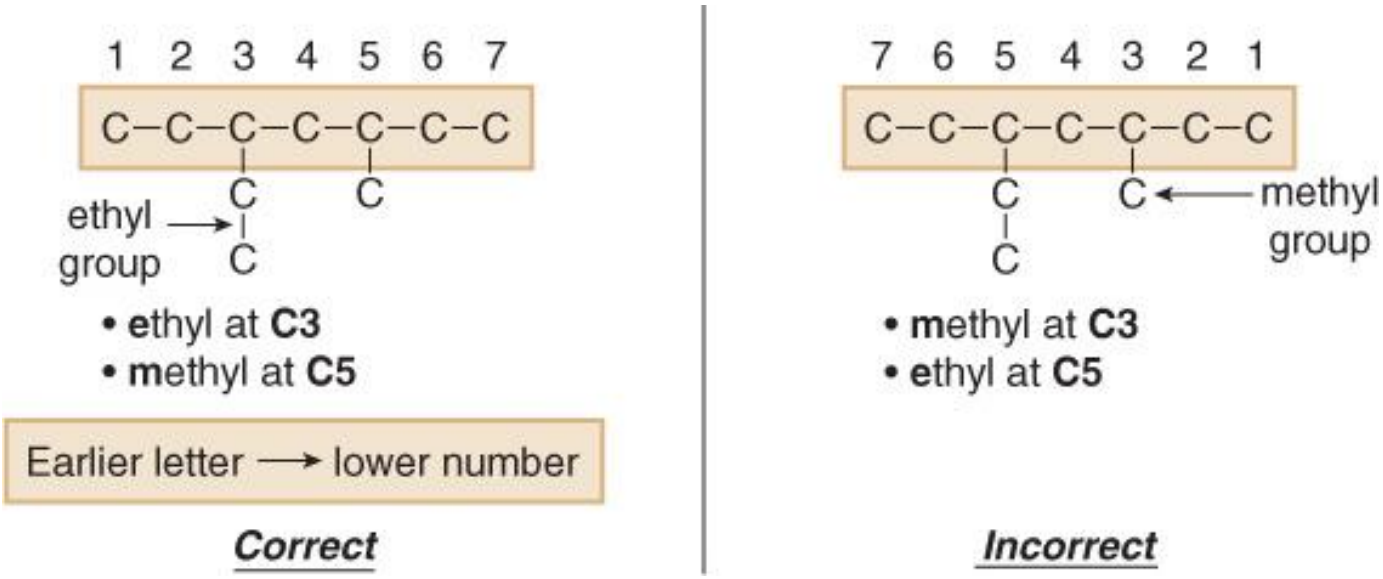




2, 3, 5

2, 4, 5

E quando há dois diferentes substituíntes equidistantes (**C3, C5 ou C5, C3**) ?



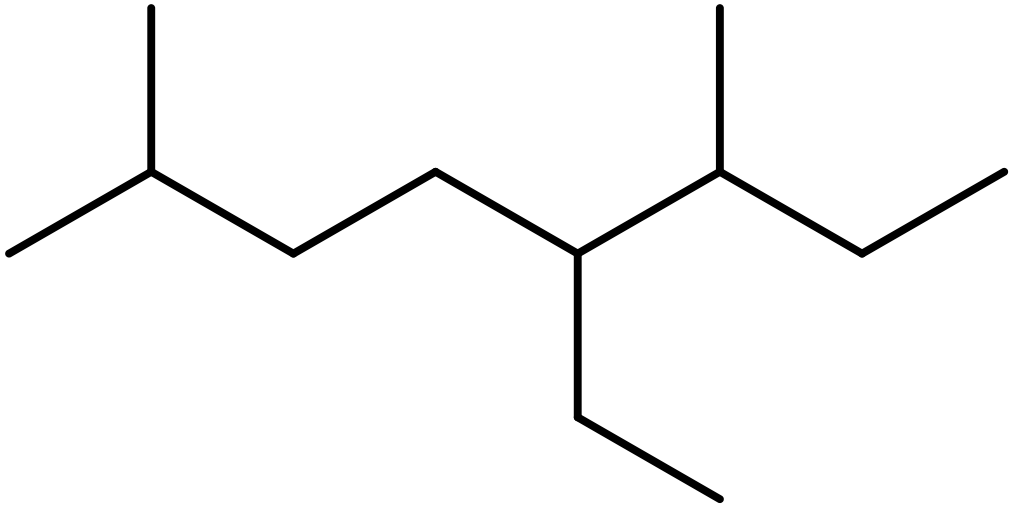
Atribua o menor número ao grupo com prioridade na ordem alfabética.

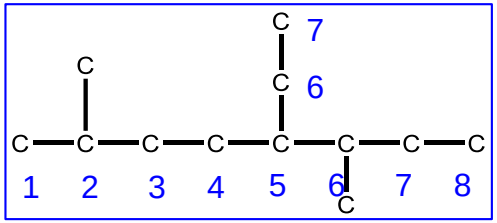
No caso, etil antes de metil.

3-etil-5-metileptano

5-etil-3-metileptano

Afinal, qual o nome do hidrocarboneto abaixo?

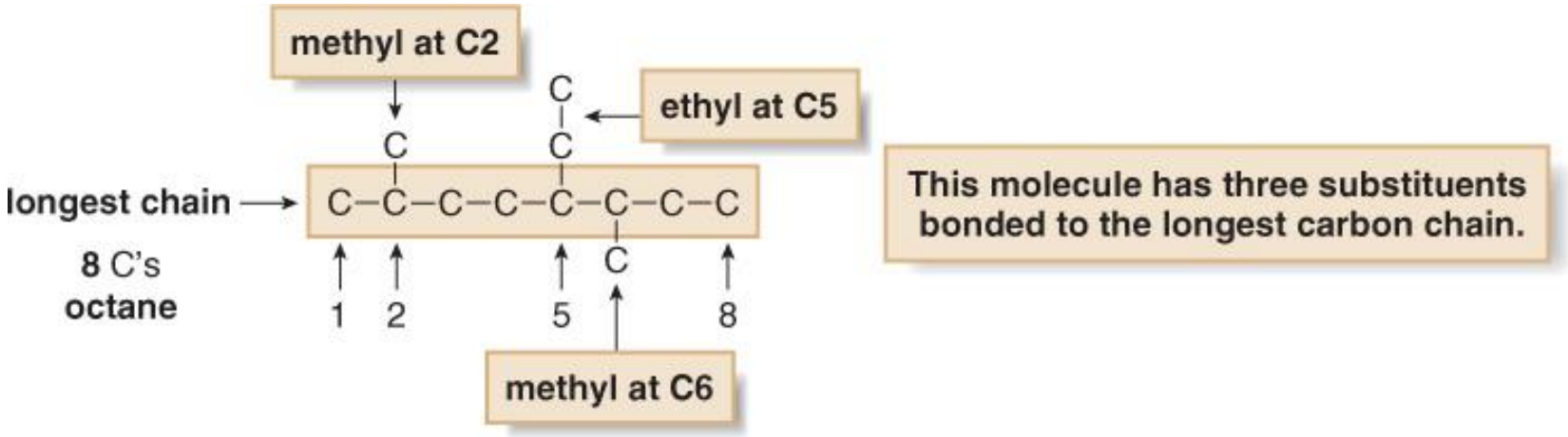




5-ethyl-2,6-dimethyl-octane

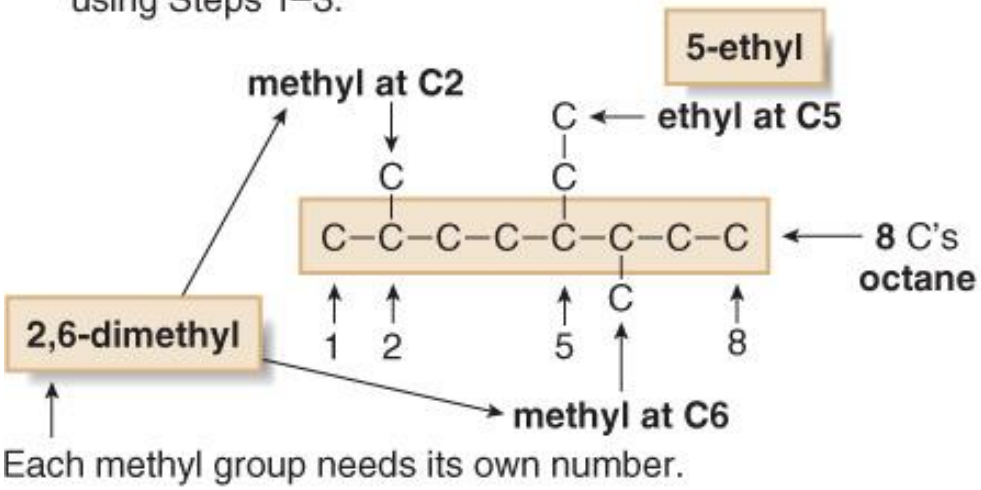
Name and number the substituents.

- Name the substituents as alkyl groups.
- Each substituent needs its own number.
- Use prefixes to indicate how many identical groups are present: di-, tri-, tetra- and so forth.



Combine substituent names and numbers + parent and suffix.

[1] Identify all the pieces of a compound, using Steps 1–3.



[2] Then, put the pieces of the name together.

substituent names and numbers + parent + suffix

5-ethyl-2,6-dimethyl + **oct** + **ane**

Alphabetize: **e** for **ethyl**, then **m** for **methyl**

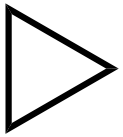
8 C's

an **alkane**

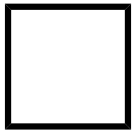
5-ethyl-2,6-dimethyl-octane

Nomenclature for cycloalkanes

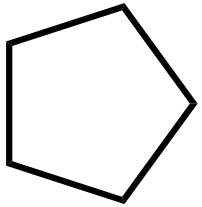
Use prefix cyclo- immediately precedes the name of the parent.



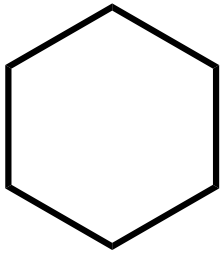
ciclopropano



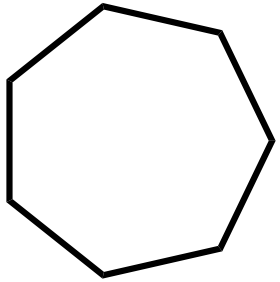
ciclobutano



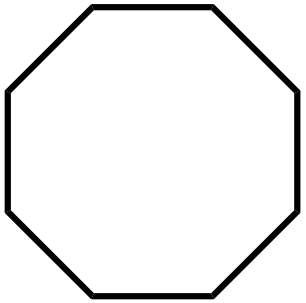
ciclopentano



ciclohexano



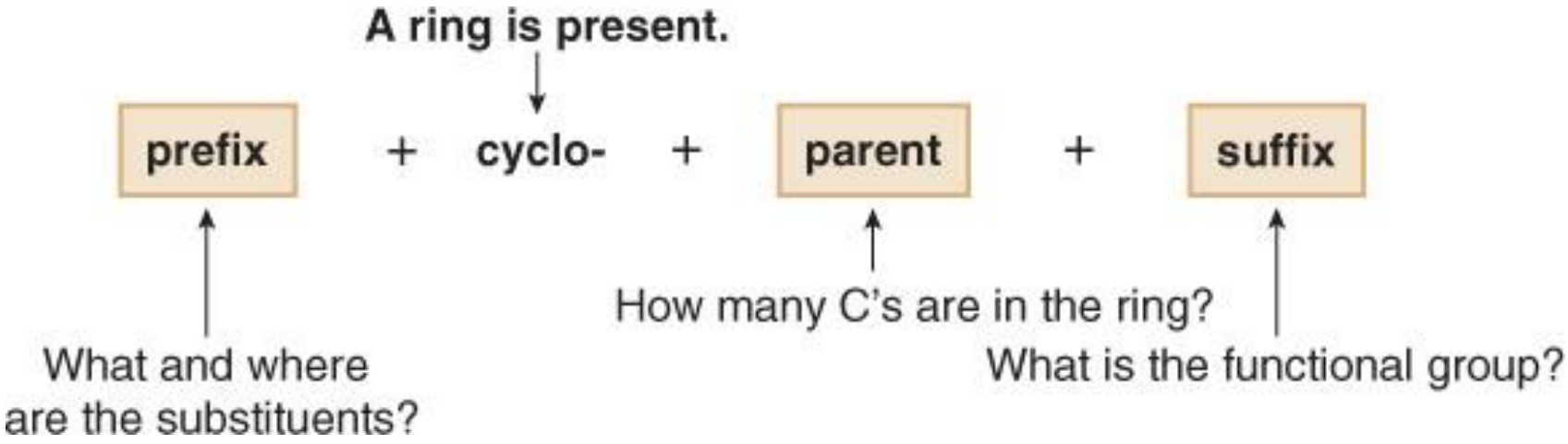
cicloheptano



ciclooctano

Nomenclature for cycloalkanes

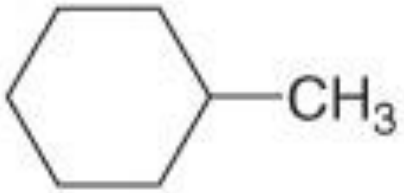
Use prefix cyclo- immediately precedes the name of the parent.



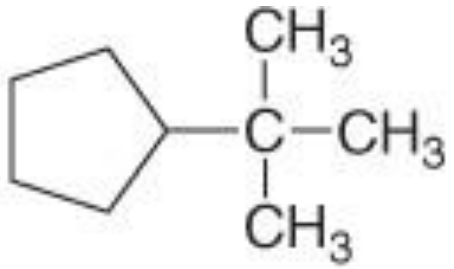
Nomenclature of cycloalkanes

Name and number the substituents.

No number is needed to indicate the location of a single substituent.

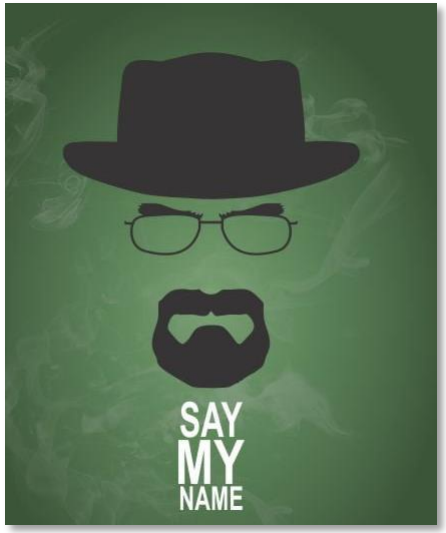


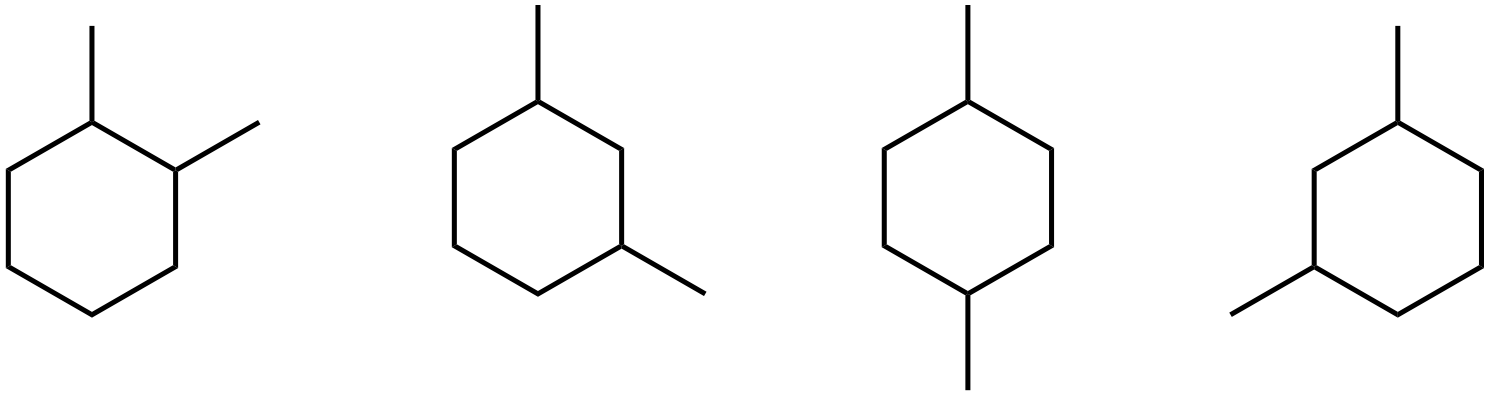
methylcyclohexane



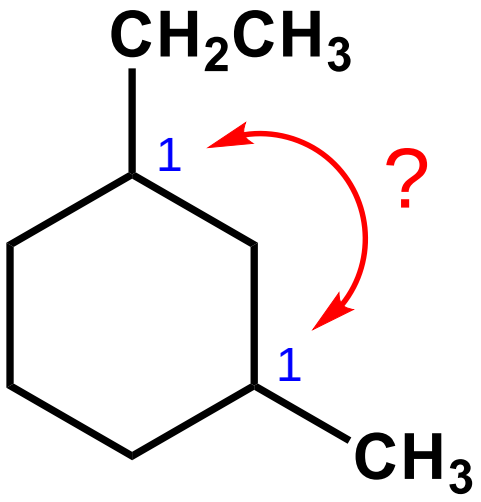
tert-butylcyclopentane

But with **two substituents**, you have to number the ring.

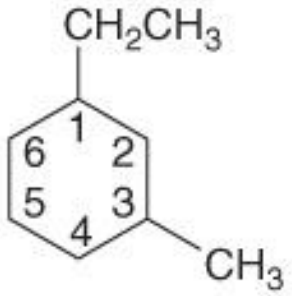

SAY
MY
NAME



Say my name



Begin numbering at the ethyl group.

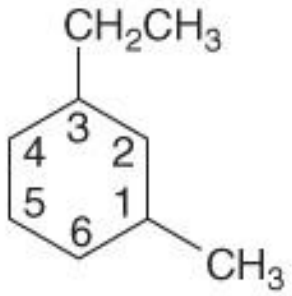


- **e**thyl group at **C1**
- **m**ethyl group at **C3**

earlier letter ⟶ lower number

Correct: **1-ethyl-3-methylcyclohexane**

Begin numbering at the methyl group.



- **m**ethyl group at **C1**
- **e**thyl group at **C3**

Incorrect: 3-ethyl-1-methylcyclohexane

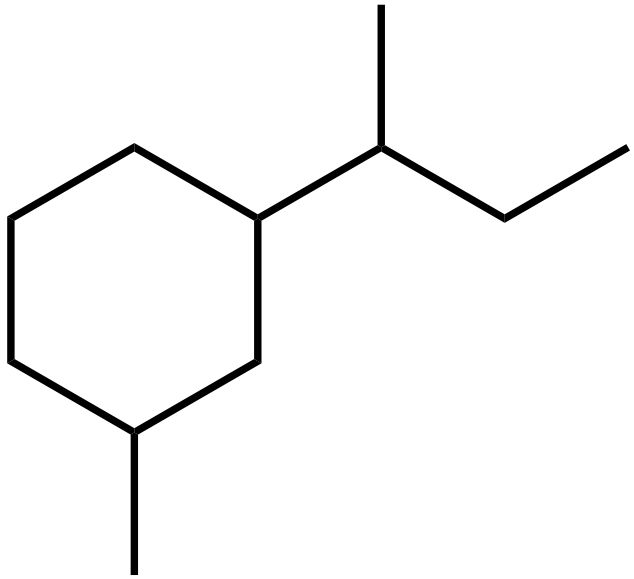
1-**e**til-3-**m**etilcicloexano

(Certo)

3-etil-1-metilcicloexano

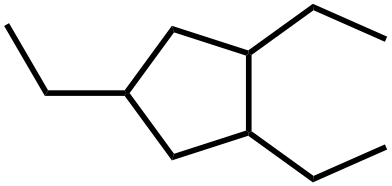
(errado)

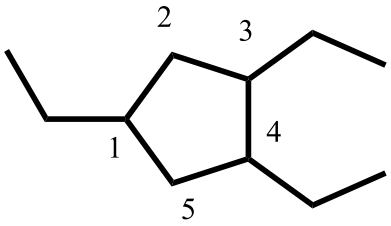
Ordem alfabética com menor numeração !!!



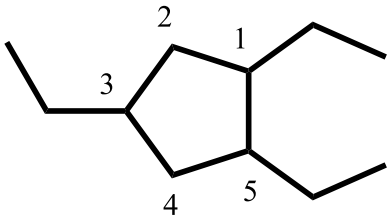
1-*sec*-**b**util-3-**m**etilcicloexano

Give the name for this cyclopentane

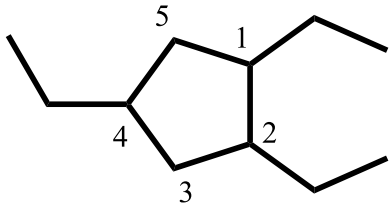




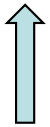
1,3,4-triethylcyclopentane



1,3,5-triethylcyclopentane

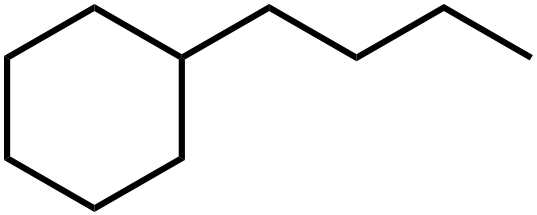


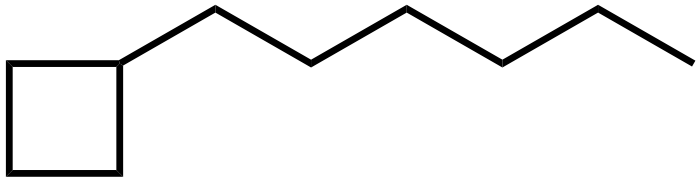
1,2,4-triethylcyclopentane



The second Et group
should be lower number

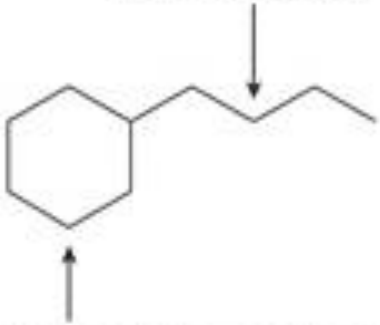
Alkane with a ring and a long chain.





more carbons in the ring

4 C's in the chain —
a **butyl** group



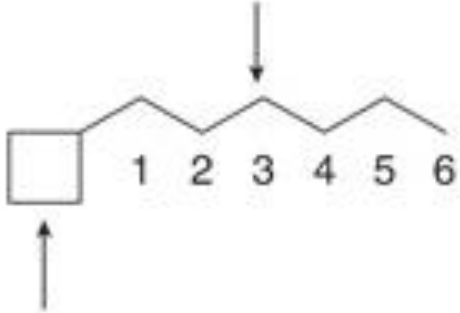
6 C's in the ring—**cyclohexane**

Name as a **cyclohexane** with a substituent.

Answer: butylcyclohexane

more carbons in the chain

6 C's in the chain —
a **hexane**



4 C's in the ring—a **cyclobutyl** group

Name as a *hexane* with a substituent.

Answer: 1-cyclobutylhexane