

## Chemistry and Introduction to Biochemistry Organic Chemistry





a fullerene

#### Some organic compounds



olive oil (including trilinoleylglycerol)

#### Carbon: the atomic " Lego"

- C can form long covalent chains giving rise to many different compounds
- C can form single, double and triple bonds C forms strong covalent bonds with H, O, S, P, N and with halogens

allotropic forms of carbon



#### Petroleum derivatives and their composition



Name	Molecular formula	Condensed structural formula
Methane	CH <sub>4</sub>	CH <sub>4</sub>
Ethane	$C_2H_6$	CH <sub>3</sub> CH <sub>3</sub>
Propane	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>
Butane	$C_4H_{10}$	$CH_3(CH_2)_2CH_3$
Pentane	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>
Hexane	C <sub>6</sub> H <sub>14</sub>	$CH_3(CH_2)_4CH_3$
Eptane	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
Octane	$C_{8}H_{18}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>
Nonane	C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>
Decane	C <sub>10</sub> H <sub>22</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>

Name	Molecular formula	Condensed structural formula
Undecane	C <sub>11</sub> H <sub>24</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>
Dodecane	$C_{12}H_{26}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>
Tridecane	$C_{13}H_{28}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub>
Tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
Pentadecane	$C_{15}H_{32}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> CH <sub>3</sub>
Hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
Eptadecane	C <sub>17</sub> H <sub>36</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub>
Octadecane	$C_{18}H_{38}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>3</sub>
Nonadecane	$C_{19}H_{40}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> CH <sub>3</sub>
Eicosane	$C_{20}H_{42}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> CH <sub>3</sub>

#### Classification of hydrocarbons



#### Molecular orbital theory (MO)

- in atoms, electrons are found in atomic orbitals
- in molecules electrons are found in molecular orbitals (Molecular Orbitals)
- using the Schrödinger equation, the shape and energies of the MOs can be calculated
  - from the combination of n atomic orbitals (mathematically a sum and subtraction of wave functions) we obtain n MO (i.e. n new wave functions)
  - 2) the MOs are ordered according to increasing energy
  - 3) the filling of the MO follows and the same rules used for atomic orbitals:
    - the principle of aufbau
    - the Pauli exclusion principle
    - Hund's rule

#### The molecular orbitals of the H<sub>2</sub> molecule



An analogy between light waves and atomic wave functions (wave-particle dualism) When light waves undergo interference, their amplitudes can add up or subtract



# The filling of the MO follows and the same rules used for the atomic orbitals

Ground state excited state  $\sigma_{1s}^*$  $\sigma^*_{1s}$ energy •H ·H H• Н 1s1s1s15  $\sigma_{1s}$  $\sigma_{1s}$ 

## Molecular orbitals from combinations of p atomic orbitals and $\pi$ molecular orbitals

Coaxial combination of atomic orbitals to form molecular  $\sigma$  orbitals can take place with other orbitals (p, sp, sp<sup>2</sup> and sp<sup>3</sup>) sp<sup>3</sup>)



By lateral overlap of 2 p orbitals, the molecular  $\pi$  orbital is obtained



Hybridization of orbitals (L. Pauling) predicts:

• 3 hybrid orbila:

- sp<sup>3</sup> (1 s orbital + 3 p orbitals)
- sp<sup>2</sup> (1 s orbital + 2 p orbitals)
- sp (1 s orbital + 1 p orbital)

the superposition of hybrid orbitals produces 2 types of bonds depending on the geometry of the overlap:

- $\sigma$  bonds formed by coaxial overlap
- $\pi$  bonds formed by lateral overlap

## sp<sup>3</sup> hybrid orbitals (all alkanes)

- 1 2s orbitals and 3 2p orbitals mix to give 4 sp<sup>3</sup> orbitals
- each sp<sup>3</sup> hybrid orbital has 2 lobes of different size
- the sign of the wave function is positive in a lobe, negative in the other and it is null to the core
- the 4 sp3 hybrid orbitals are directed to the vertices of a regular tetrahedron regular with 109.5  $^{\circ}$  angles



4 sp<sup>3</sup> tetrahedral hybrid orbitals

## sp<sup>2</sup> hybrid orbitals (alkenes & arenes)

- 1 2s orbital and 2 2p orbitals mix to give 3 sp<sup>2</sup> orbitals 1 unhybridized 2p orbital remains
- each sp<sup>2</sup> hybrid orbital has 2 lobes of different size
- the axes of the 3 sp<sup>2</sup> hybrid orbitals lie on a plane and are directed to the vertices of an equilateral triangle with angles of 120
- the non-hybridized 2p orbital is perpendicular to the plane of 3 sp<sup>2</sup> hybrid orbitals



### Sp hybrid orbitals (presenti in tutti gli alchini)

- 1 2s orbital and 2 2p orbitals mix to give 2 sp orbitals 2 unhybridized 2p orbitals remain
- each sp hybrid orbital has 2 lobes of different size
- the 2 sp orbitals are coaxial (180  $^{\circ}$  angle)
- he 2 non-hybridized 2p orbitals are perpendicular to each other and perpendicular to the axis that connects the 2 orbitals sp



### Ways of representing organic molecules

Ball and stick model



lines and angles formula (stick)





shortened structural formula

 $\mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_3$ 

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

propan3 (C<sub>3</sub>H<sub>8</sub>)

buthane  $(C_4H_{10})$ 

pentane ( $C_5H_{12}$ )

#### Hydrocarbons

They can be divided into four large groups:

1 aliphatic: open chain, linear or branched, saturated or unsaturated

2 cyclic

3 aromatic: contain at least one benzene ring

4 heterocyclic: containing atoms other than carbon in the ring



#### Alkanes

Names, molecular formulas and abbreviated structural formulas of the first 20 linear alkanes( $C_n H_{2n+2}$ )

name	molecular formula	abbreviated structural formula	name	molecular formula	abbreviated structural formula
methane	CH <sub>4</sub>	CH <sub>4</sub>	undecane	$C_{11}H_{24}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>
ethane	$C_2H_6$	CH <sub>3</sub> CH <sub>3</sub>	dodecane	$C_{12}H_{26}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>
propane	$C_3H_8$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	tridecane	$C_{13}H_{28}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub>
butane	$C_{4}H_{10}$	$CH_3(CH_2)_2CH_3$	tetradecane	$C_{14}H_{30}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CH <sub>3</sub>
pentane	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	pentadecane	C <sub>15</sub> H <sub>32</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> CH <sub>3</sub>
hexane	$C_{6}H_{14}$	$CH_3(CH_2)_4CH_3$	hexadecane	$C_{16}H_{34}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CH <sub>3</sub>
eptane	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	eptadecane	$C_{17}H_{36}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub>
octane	C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	octadecane	$C_{18}H_{38}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>3</sub>
nonano	C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	nonadecane	C <sub>19</sub> H <sub>40</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> CH <sub>3</sub>
decane	$C_{10}H_{22}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	eicosane	$C_{20}H_{42}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> CH <sub>3</sub>

#### Physical properties of alkanes

They are non-polar molecules, less dense than the water in which they are insoluble.

Intermolecular attractions are due to weak van der Waals forces, the stronger the larger the molecule.

Name	abbreviated structural formula	melting point (°C)	boiling point (°C)	density (g/mL a 0 °C)
methane	CH <sub>4</sub>	-182	-164	(gas)
ethane	CH <sub>3</sub> CH <sub>3</sub>	-183	-88	(gas)
propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	-190	-42	(gas)
butane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	-138	0	(gas)
pentane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	-130	36	0.626
hexane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	-95	69	0.659
eptane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	-90	98	0.684
octane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	-57	126	0.703
nonane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	-51	151	0.718
decane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	-30	174	0.730



$$\delta^{25 \ \circ C} = 0.655 \ g/mL$$

$$\delta^{25 \ \circ C} = 0.997 \ g/mL$$

$$\delta^{25 \, ^{\circ}\mathrm{C}} = 1.584 \, \mathrm{g/mL}$$

#### IUPAC nomenclature of alkanes

- 1. the longest possible linear chain is chosen as the basic structure.
- 2. the compound is considered as derived from this structure by substitution of hydrogen atoms with alkyl groups (see below).
- 3. the carbon atoms of the main chain are numbered starting with from the extremity that allows to use the lower numbers to indicate the substituents.
- 4. if the same group appears more than once as a side chain, the prefix di-, tri-, tetra-, etc. is added.
- 5. if there are different alkyl groups linked to the main chain, they are listed in alphabetical order.

The branched alkanes can be considered as derived from a linear alkane by substitution of a hydrogen atom with an alkyl group



Name the following compound C<sub>8</sub>H<sub>18</sub>



It is a substituted hexane



There are 2 methyl groups in positions 2 and 4

This is 2,4-dimethylhexane

Classification of carbon atoms A carbon atom can be: primary, secondary, tertiary or quaternary, depending on whether it binds 1, 2, 3 or 4 other carbon atoms.



Example: What is the systematic name of the following hydrocarbon?



• he longest linear alkane contains 12 carbon atoms  $\rightarrow$  dodecane

- there is an ethyl group in position 4
- there are 4 methyl groups in positions 2, 3, 5 and 9

The alkane is therefore 4-ethyl-2,3,5,9-tetramethyldodecane.



#### Isomerism

Isomerism (from the Greek  $\upsilon\sigma\sigma\sigma$ , equal,  $\mu\epsilon\rho\sigma\sigma$ , part) occurs when substances that differ in physical properties and often also in chemical behavior have the same brute formula, i.e. the same molecular mass and the same percentage composition. So isomers differ in how the atoms are connected.



Constitutional isomers: arrangement and bonding modalities of atoms (of structure, position, function)

Structural: different carbonaceous skeleton  $C_4H_{10}$ 

Positional: different position of functional groups C<sub>3</sub>H<sub>9</sub>N

Functional: different functional groups C<sub>4</sub>H<sub>10</sub>



ethanol

 $C_2H_6O$ 



dimethylether



2-ammino-propane



# Stereoisomers: arrangement of atoms in space (conformational, geometric, optical)



### Constitutional isomers have different physical properties

Molecular formula	Structural formula	T <sub>fus</sub> (°C)	T <sub>eb</sub> 1atm (°C)	δ <sup>20°</sup> (g/mL)
$C_6H_{14}$ $C_6H_{14}$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> I CH <sub>3</sub>	-95 -153.7	68.7 60.3	0.6594 0.6532
$C_6H_{14}$	CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>2</sub> CH <sub>3</sub> I CH <sub>3</sub>	-118	63.3	0.6643
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> CH—CHCH <sub>3</sub> I I CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	-128.8	58	0.6616
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> H CH <sub>3</sub> -C-CH <sub>2</sub> CH <sub>3</sub> CH <sub>3</sub>	-98	49.7	0.6492

in order: n-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane

There are no constitutional isomers for methane, ethane and propane. These increase rapidly as the number of carbon atoms increases

Molecular formula	number of possible constitutional isomers
$C_4H_{10}$	2
$C_{5}H_{12}$	3
$C_6H_{14}$	5
$C_7H_{16}$	9
$C_8H_{18}$	18
$C_{9}H_{20}$	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4347
C <sub>20</sub> H <sub>42</sub> (eicosane)	366 319
C <sub>30</sub> H <sub>62</sub> (triacontane)	4 111 846 763
$C_{40}H_{82}$ (tetracontane)	62 481 401 147 341

Example: How many isomers are possible for pentane  $(C_5H_{12})$ ?





### The conformation of a molecule

The conformation of a molecule is the spatial arrangement that the atoms of a molecule assume upon rotation around simple bonds ( $\sigma$ ). Each conformation that the molecule can assume is also called the conformational isomer, conformer (rotamer).

In the great majority of cases, at room temperature the conformations rapidly interconvert into each other and it is not possible to isolate a single conformer, however there may be cases in which the steric hindrance is such as to block the molecule in one of the possible conformations .

#### **Conformational changes are of paramount importance in biology:**

- protein folding is a complex conformational process
- during the catalytic cycle many enzymes necessarily change their conformation
- DNA can take on different conformations
- allosteric proteins (hemoglobin)

The DNA double helix can take on different conformations, which can affect DNA-protein recognition. The relative dimensions of the major and minor sulcugrooves vary with the type of conformation



 $A = 11 \text{ base/turn } (24.6\text{\AA}) - \text{diameter } 26 \text{\AA} - \text{right-handed} \\ B = 10 \text{ base/turn } (33.2\text{\AA}) - \text{diameter } 20 \text{\AA} - \text{right-handed} \\ Z = 12 \text{ base/turn } (45.6\text{\AA}) - \text{diameter } 18 \text{\AA} - \text{left-handed}$ 



The peptide bond and the solid angles  $\phi$  and  $\psi$ 

φ: rotation around the amide  $C_α$ -N bond ψ: rotation around the amide  $C_α$ -C bond

The numerical values of the dihedral angles identify the conformation of the polypeptitide

#### The conformations of ethane $(C_2H_6)$



Due to the reciprocal electrostatic repulsion between the electrons, ethane tends to preferably assume a staggered conformation



rotation



The Rieske protein in Complex III can adopt at least two stable conformations



from yeast structure 1KY0

The Rieske protein in Complex IIIcan adopt at least two stable conformations



from beef structure 1BE3

#### b conformation



 $c_1$  conformation



intramolecular ET between docked  $c_1$ and FeS takes place