The chemical building blocks of life

Carbon, water and possible alternatives

Planets and Astrobiology (2018-2019)
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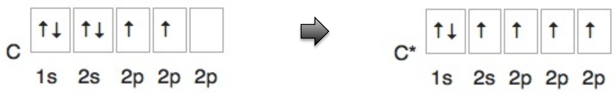
Carbon

In terrestrial life carbon is the building block of biological molecules

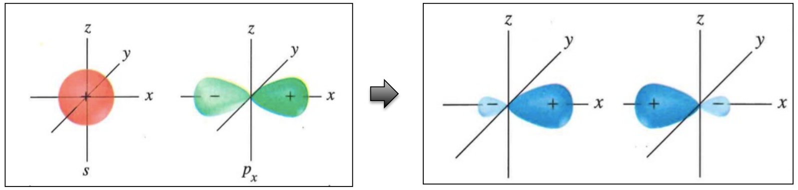
- With respect to other cosmically abundant atoms, carbon offers several advantages in terms of structural and metabolic properties
- Electronic configuration
  - Carbon's ground state configuration is $1s^2\ 2s^2\ 2p^2$



  - The excitation of one electron of the 2s orbital easily provides a configuration with 4 orbitals with a single electron
  - From a quantum mechanical point of view the linear superposition of the wave functions associated with the 2s and 2p orbitals provides a variety of hybrid orbitals

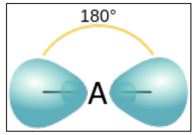
Hybridization of carbon valence orbitals

sp orbitals: two atomic orbitals are mixed to form two hybrid orbitals



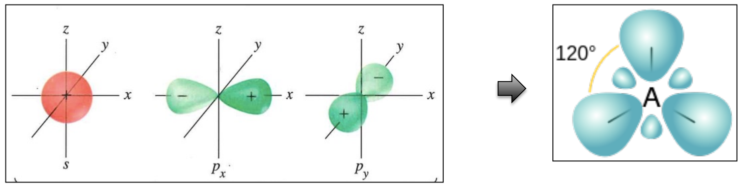
The two sp hybrid orbitals arrange themselves in three dimensional space to get as far apart as possible with a bond angle of 180º.

The geometry which achieves is linear.

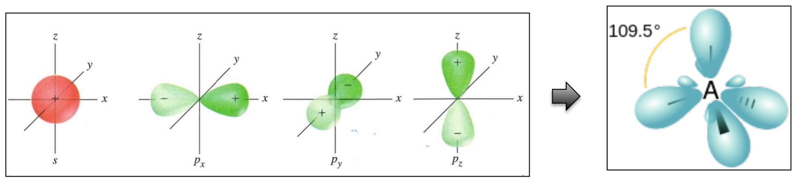


Hybridization of carbon valence orbitals

sp^2 orbitals: three atomic orbitals are mixed to form three hybrid orbitals



sp^3 orbitals: four atomic orbitals are mixed to form four hybrid orbitals

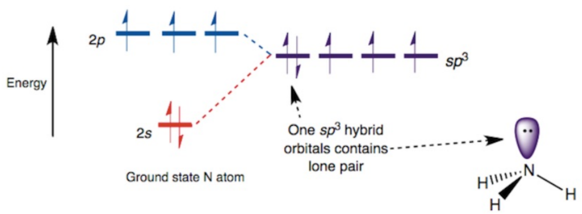


Carbon

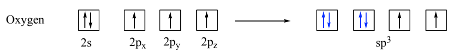
- Structural properties
  - In summary, carbon has 4 oriented covalent bonds that allow the formation of a great variety of 3D molecular structures
  - The valence orbitals 2s and 2p can hybridize forming:
    - two sp hydrid orbitals ➔ linear structures
    - three sp^2 hybrid orbitals ➔ planar structures
    - four sp^3 hybrid orbitals ➔ tetrahedrical structures
  - The same flexibility of forming geometrical structures is not found in other atoms

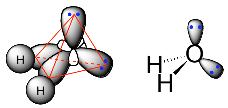
Carbon versus nitrogen and oxygen

Nitrogen has 3 covalent bonds which tend to form planar structures



Oxygen has 2 covalent bonds which tend to form linear structures

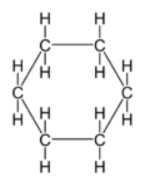




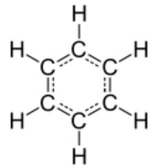
Organic ring structures

Carbon can form a variety of ring structures

Carbon is the only atom with the capability of forming aromatic rings



Cyclohexane (saturated molecule)



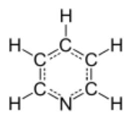
Aromatic ring of Benzene (unsaturated molecule)

Hetero-organic molecules

- Carbon is capable of forming complex molecules not only with itself, but also with H, O and N

This is because the bonds C-C, C-H, C-O, and C-N have similar energies

For instance, N can replace C in ring structures



The large flexibility of carbon in terms of geometrical structure, coupled with the possibility of substitutions of other abundant elements, leads to a infinite number of possible molecular structures potentially suitable for different biological functions

Advantages of carbon

- Metabolic properties
  - Carbon can easily be transformed from the completely oxidized form, CO_2, to the completely reduced form, CH_4
    - This is an advantage for the capability of activating metabolic processes, which are largely based on redox reactions
    - This provides the possibility of cycling carbon between its "inorganic form" and its "organic form"

CO_2: "inorganic carbon"

CH_4: "organic carbon"

Silicon versus carbon

Silicon and carbon lie in the same column of the Periodic Table

- Silicon has been proposed as a possible alternative for biological molecules

Silicon based chemistry, however, is by far less flexible than carbon chemistry

- Si is not able to form double covalent bonds with the same easiness as C
- The larger volume occupied by the external electronic orbitals of silicon tend to reduce the superposition of *p* orbitals

The properties of silicon and carbon are quite different in many respects

- For instance, the electronegativities (i.e. the tendency to attract electrons) are different
- According to the Pauling's scale of electronegativity:

$\chi(H)=2.2 \qquad \chi(C)=2.55 \qquad \chi(Si)=1.90$

- As a result, the polarities of C–H bond are inverted compared to the polarities of Si–H bonds

δ^- C–H δ^+ $\qquad$ δ^+ Si–H δ^-

Role of silicon in biochemistry

Due to its electronegativity, lower than that of hydrogen, silicon is not able to participate in hydrogen bonding

Therefore, silicon cannot play a role in the chemical groups involved in intermolecular, hydrogen-bond interactions essential for life molecular processes, such as intermolecular recognition, molecular replication, or molecular folding

The example of terrestrial life shows that silicon can play other roles in living organisms, typically related to structural support

- One of the best examples is the presence of silicates in the shells of diatoms (unicellular algae)
- Silicon, in different forms, is employed also by plants (e.g., to form rigid protrusions) and animals (e.g., in hair, nails, and bones)

The larger flexibility of carbon, compared to silicon, is supported by astronomical observations of interstellar molecules

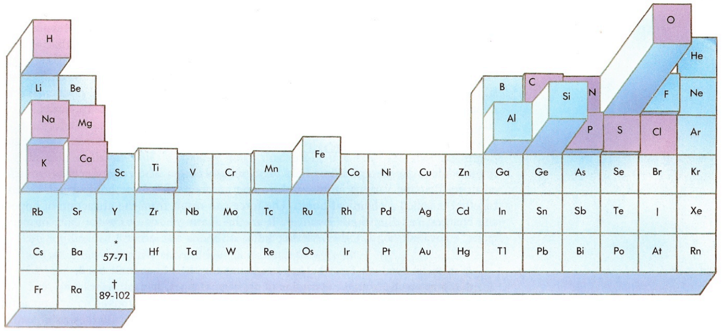
- Complex gas-phase molecules based on Si have not been found
- Si tends to be incorporated in the form of silicates in the refractory component of dust grains

Table 5.4 Some complex carbon compounds detected in the interstellar medium and meteorites.

Number of Atoms				
6	7	8	9	> 9
C_5H, HCH_2OH	CH_3C_2H	CH_3OCHO	$(CH_3)_2O$	$(CH_3)_2CO$
NH_2CHO,	CH_3CHO	CH_3C_3N	CH_3CH_2OH	HC_9N
CH_3CN	HC_5N, C_6H	C_7H, H_2C_6	CH_3CH_2CN	$HC_{11}N$
CH_3NC,	CH_3NH_2		HC_7N	C_6H_6, C_{60}^+
CH_3SH	CH_2CHCN		CH_3C_4H, C_8H	PAHs,
H_2C_4,	C_2H_4O		CH_3C_4N	glycine?
HCC_2HO,				
C_5H, C_5N,				
C_5O				

The chemical abundances of elements in the Earth crust provide indirect evidence on the relative importance of silicon and carbon

Legenda: the biological elements are shown in pink color
Abundances in the earth crust are indicated by the height of boxes

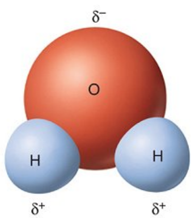


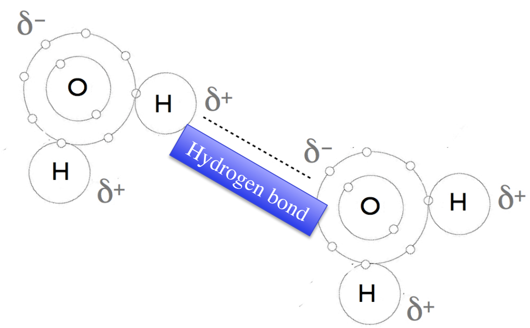
Despite the highest abundance of silicon, terrestrial life has "chosen" carbon

This provides further evidence that carbon-based biochemistry is more flexible than silicon-based biochemistry

The water molecule

Water, the most abundant molecule in terrestrial life, is a polar molecule
Its capability of hydrogen bonding is strictly related to its polarity

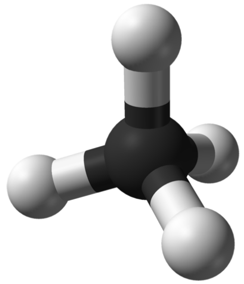




Polar and non-polar molecules

- The polar character depends on the geometrical distribution of electric charges of the molecule
  Water is polar because of the asymmetric distribution of charges
  Methane is non polar (no electric dipole)

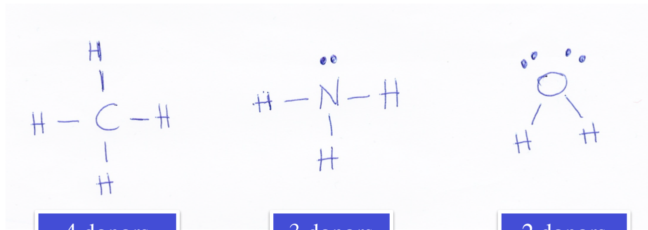
Methane:
a non-polar molecule



- Polar molecules
  - can be solved in water
  - are hydrophilic
- Non-polar molecules
  - cannot be solved in water
  - are hydrophobic

The medium of life in exobiology: water versus other solvents

Among cosmically abundant molecules,
water has the highest capability of hydrogen bonding



4 donors no acceptors | 3 donors 1 acceptor | 2 donors 2 acceptors

As a result, water has the capability of forming
a molecular network that supports and actively interacts
with the molecules specialized in genetic and catalytic properties

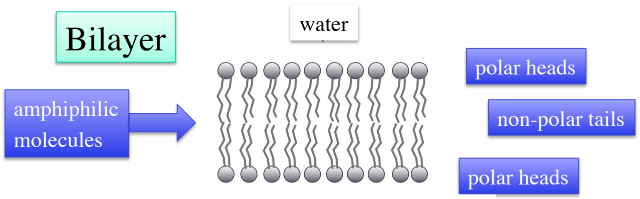
Properties of water relevant to life (1)

- The water molecule has a high electric dipole
  - Water is a good solvent

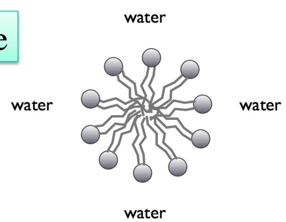
    Thanks to this property, the dissolved molecular constituents have the mobility required for metabolic processes to take place
  - Thanks to the polarity, amphiphilic molecules in water can spontaneously form structures of biological interest (bilayers, micelles)

Polar molecules allow spontaneous formation of molecular structures of biological interest

Bilayer



Micelle



Geometrical configurations with lowest potential energy

Properties of water relevant to life (2)

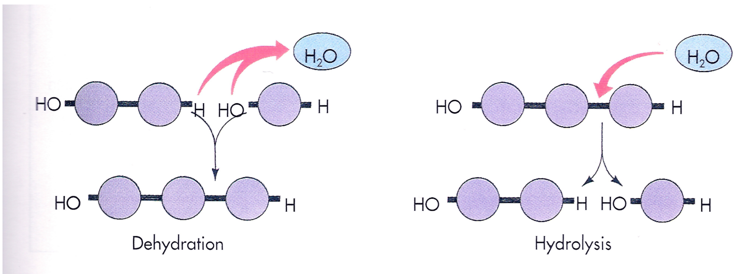
- Water spontaneously form ions
  - Spontaneous breaking of covalent bonds in a small fraction of water molecules yields H^+ and OH^- ions

Note: the concentration of H^+ ions in water is used to define the pH scale

The free ions, and in particular H^+, can be used to transport electric charges

H^+ and OH^- take part in metabolic reactions

- Water takes part of fundamental metabolic processes, both as a reactant and as a product of reaction
- Water formation and dissociation has the potential to play an important role in metabolic processes, as it does in terrestrial life



Comparison of water with other molecules

Main properties of water and of some polar or non-polar molecules

Proprietà	Note	H_2O	NH_3	HCN	HF	H_2S	CH_3OH	N_2H_4	CH_4	C_2H_6
μ	(a)	18.0	17.0	27.0	20.0	34.1	32.0	32.1	16.0	30.1
ρ	(b)	0.997	0.696	0.684	0.818	1.393	0.793	1.00	0.426	0.572
p	(c)	1.85	1.46	2.99	1.83	0.98	1.6	1.9	0.00	0.00
T_{fus}	(d)	0	−78	−13	−83	−86	−94	2	−182	−172
T_{boil}	(d)	100	−33	26	20	−60	65	114	−162	−89
ΔT_{liq}	(e)	100	44	39	103	26	159	111	20	83
ΔH_{vap}	(f)	40.7	23.3	25.2	30.3	18.7	40.5	40.9	8.2	14.7
$\Pi_i a_i$	(g)	−3.4	−4.3	−7.9	−7.6	−4.9	−7.1	−8.5	−3.8	−7.5

(a) Peso molecolare in unità di masse atomiche. (b) Densità in g/ml. (c) Momento di dipolo in debye (1 D = 10^{-10} esu · Å). (d) Punti di fusione e di ebollizione in °C alla pressione di 1 bar. (e) Intervallo di temperature in cui il composto è in fase liquida alla pressione di 1 bar. (f) Entalpia di vaporizzazione in kJ/mol. (g) Disponibilità cosmica.

Critical factors:
polarity, liquid phase interval, specific heat, cosmic abundance

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The comparison with other molecules generally favours water as an optimal medium for life

For instance other polar solvents, such as HF, are interesting in principle, but are by far less abundant than water in the cosmos.
Here the index in the row (g) represents the product of the cosmic abundances of the atoms that compose the molecule.

Water also has a relatively high specific heat, which is useful to stabilize the temperature of living systems.

Ammonia

- NH_3 is polar, with polar strength similar to that of H_2O
  - The weaker capability of hydrogen bonding (compared to water) makes ammonia less ideal to form of a molecular network able to support interactions between biomolecules
- NH_3 is liquid at lower temperatures than water
  - An hypothetical life with liquid ammonia as a medium would operate at low temperatures, meaning slow chemical reactions and low thermal energy
- Like water, ammonia undergoes molecular autoionisation to form its acid and base conjugates:
  - 2 NH_3 (aq) ←→ NH_4^+ (aq) + NH_2^- (aq)
- These ions are larger than H^+ and OH^- ions and are less suitable for charge transportation and for taking part in metabolic pathways

Hydrazine

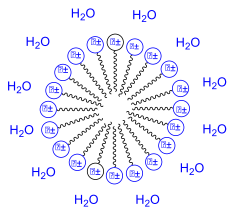
- N_2H_4 is liquid in a broad range of temperatures and is an excellent polar solvent, with polar strength similar to that of H_2O
- Also its dielectric constant and viscosity are very similar to water
- Hydrazine is a very reactive molecule and decomposes extremely fast in the presence of oxygen, making it an ideal rocket fuel, but not a good solvent for life in the presence of oxygen
  - Low temperatures in an anoxic environment perhaps would be conducive to controlled biochemical reactions at a reasonable speed
  - Hydrazine is not an abundant molecule
- In summary, hydrazine does not appear to be a promising solvent candidate despite having some favourable properties

Non-polar hydrocarbons

- CH_4 and C_2H_6 are non polar
  - They are not able to form a network of hydrogen bonds able to support the interactions between genetic and catalytic molecules
- They are liquid at very low temperatures
  - An hypothetical life based on liquid CH_4 and C_2H_6 would be characterized by very slow chemical reactions and very low thermal energy

- In principle, micelles and bilayers could still be formed in liquid hydrocarbons
  - with reversed shape, if we use amphiphilic molecules with polar heads
  - with “typical” shape, if we use amphiphilic molecules with non-polar heads

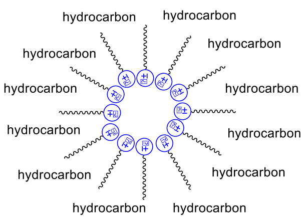
+ Typical micelle (in water)



+ Typical surfactant: polar head, lipophilic tail

Facchin, Perosa, Riello (2015)

Inverse aggregate (e.g. micelle in hydrocarbon)



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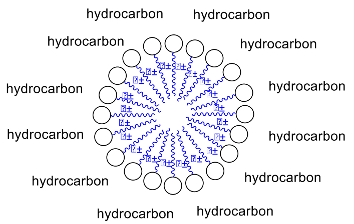

- Reverse surfactant: lipophilic head, polar tail