

ORGANIC AND BIO-MOLECULAR CHEMISTRY

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Summary

Organic and Bio-Molecular chemistry is the discipline that studies the molecules of life, which are made by carbon atoms, and includes also all the synthetic compounds the skeletons of which contain carbon atoms. Living organisms are “built up and organized” exploiting compounds the skeleton of which is mainly made up of carbon atoms. The study of these compounds, defined Natural Compounds, as far as structure, properties and biological role is concerned, is the subject matter of Organic and Bio-Molecular Chemistry. Chemists have been able to synthesize a great variety of new compounds with a skeleton mainly based on carbon atoms; these new molecules also belong to the class of Organic Compounds. The carbon skeleton of organic compounds represents the stable scaffold, in which the presence of multiple bonds and heteroatoms, mainly oxygen, nitrogen, sulfur, and phosphorus, eventually allow the organic molecule to perform “functions” such as molecular interactions and reactivity. For this reason these groups are defined as functional groups and give rise to the most common classification of organic compounds. Organic chemistry studies the structure, nomenclature, physico-chemical properties and reactivity of each single class of organic compounds. Particular attention is devoted to organic compounds of living organisms, such as carbohydrates, amino acids and proteins, nucleic acids, lipids; they perform all structural and/or functional roles that allow an organism to live and reproduce. Organic compounds have

also an important role in the market, and the chemical industries strongly contribute to the economy of industrialized countries. Many organic compounds such as polymers, dyes, compounds for health care such as medicinal drugs and cosmetics, compounds for food industry such as sweeteners, nutraceuticals, preserving agents, emulsifiers and stabilizers, are widely used and contribute to our quality of life. The extensive production and use of synthetic organic compounds has generated some environmental problems, therefore particular attention is devoted to environmentally safe production processes and biodegradable organic polymers. Organic and Bio-Molecular chemistry also studies how to isolate organic compounds from a mixture, how to determine the chemical structure and how to detect purity. A variety of instrumental techniques have been developed for these purposes; it is now possible to detect the presence of organic compounds, even in traces, and to determine their chemical structure.

1. Introduction

Chemistry is the discipline that studies the structure, properties, and methods of manipulation and transformation of all materials around us, from simple gases present in the air, nitrogen and oxygen, to the strangest and most complex compounds produced by microorganisms. Organic and Bio-Molecular Chemistry concerns in particular, as indicated by the name, the wide variety of compounds that constitute the living organisms; it includes however also structurally related compounds that have been mass-produced in laboratories and by industry in the 20th century.

The origin of modern Organic Chemistry can be dated at the beginning of the 19th century, when scientists such as Gay-Lussac (1810) and Berzelius (1814) developed methods of analysis of the compounds derived from living organisms, allowing a systematic study which put into evidence the common characteristics of these compounds, that have been classified as “organic compounds”. For a long time it was believed that organic compounds were generated in Nature by a sort of magic “vital force”, despite the fact that in 1828 Wöhler was able to demonstrate that the urea produced in the laboratory by heating ammonium cyanate, an inorganic compound, was identical to the urea of natural origin.

Looking for a common characteristic of organic compounds, it was very soon clear that there is a relevant difference in chemical composition between them and inorganic compounds. Rocks are mainly made up of Oxygen (O) and Silicon (Si) atoms (see Table 1), whereas the structure of compounds of living organisms is mainly made with Carbon (C) atoms. Table 1 describes the percentage of the different elements present in the inanimate earth with respect to the human body. Considering that one of the most abundant compounds in the human body is water (H₂O), it is clear from the Table that the most abundant element in the structure of organic compounds is Carbon.

Organic Chemistry is therefore the chemistry of carbon-containing compounds, no matter if they are natural or synthetic.

Earth		Human body	
Element	%	Element	%
O	47	H	63
Si	28	O	25.5
Al	7.9	C	9.5
Fe	4.5	N	1.4
Ca	3.5	Ca	0.31
Na	2.5	P	0.22
K	2.5	Cl	0.08
Mg	2.2	K	0.06
Ti	0.46	S	0.05
H	0.22	Na	0.03
C	0.19	Mg	0.01

Table 1: Percentage of the different elements present in the inanimate earth with respect to the human body

The evolution of Organic Chemistry has been impressive, there are practically no limits as to what can be synthesized in a laboratory; apart for very complex natural compounds, a large number of new compounds have been synthesized for different purposes. Organic compounds have a place in our everyday life; they constitute many useful materials such as plastic or fibers; they are present in food and beverages (which by the way are by definition organic compounds) as sweeteners, vitamins, flavors, coloring agents, emulsifiers, preservatives; they are used for health care, as medicinal drugs or cosmetics.

Starting from petrol, which is presently the cheapest and most abundant reserve of organic compounds, a potentially infinite number of different molecules can be synthesized, by exploiting the great variety of chemical reactions that have been developed since the 21st Century, and progress in the techniques of purification and structural determination. On the other hand, the molecular mechanisms of life, all involving organic compounds, from complex proteins to very small neurotransmitters such as acetylcholine or noradrenaline, have been largely elucidated. Proteins, carbohydrates, nucleic acids, lipids, products of the secondary metabolism, and more in general organic compounds of the biological systems, are specifically defined “bio-molecules” and the branch of organic chemistry that studies the nature of these bio-molecules and their behavior in the organism, is defined “bio-molecular chemistry”

2. The Carbon Atom

The Carbon atom is the main constituent of organic molecules, as shown in Table 1, whereas the Silicon atom is the main component of rocks. Why? Why are rocks mainly built-up of Silicon and Oxygen atoms whereas Nature has selected the Carbon atom for living organisms? Silicon and Carbon have a common feature: they are “tetravalent”, in other words they are like scaffolds that can be elongated in four directions. Silicon and Carbon atoms can establish four molecular bonds, represented with a line in Figure 1, each of which links a different atom. Four linkages with different atoms is the highest possibility for the most abundant elements present in the earth; hydrogen and chlorine

are monovalent, they can establish only one linkage; oxygen is bivalent, it establishes two linkages; nitrogen, boron and aluminum are trivalent, they can establish three linkages with different atoms. Therefore silicon and carbon, the two abundant tetravalent elements, are the most efficient scaffolds to build up tridimensional molecular structures. There is however an important difference between silicon and carbon: the energy of C-C linkage is around 80-90 kcal/mol, whereas the Si-Si linkage is much weaker, 53 kcal/mol, which makes it very unstable. On the other hand, the Si-O bond is very strong (108 kcal/mol), therefore very stable molecular architectures can be generated intercalating Si and O atoms as shown in Figure 1 for silicates. This kind of structure is so stable, let us say “static”, to be inadequate for living organisms which require more “dynamic” compounds. Living organisms generate fructose, an organic compound with a six carbon atom chain, from carbon dioxide and water, in a process defined as photosynthesis which exploits the energy of the sun. Fructose undergoes metabolic transformations to generate other organic compounds. It is clear therefore that organic molecules must be “dynamic”, as they must be generated (biosynthesized) and transformed (metabolized) by cleavage of some bonds and formation of new ones. The carbon atom is much more suitable for this purpose, 80-90 kcal/mole of the C-C bond is the strength of choice, not too strong and not too weak; therefore it has been selected in Evolution to generate organic compounds. Palmitic acid, in Figure 1, present in palm tree oil, is an interesting example of an organic compound in which sixteen carbon atoms are linked together generating a long chain.

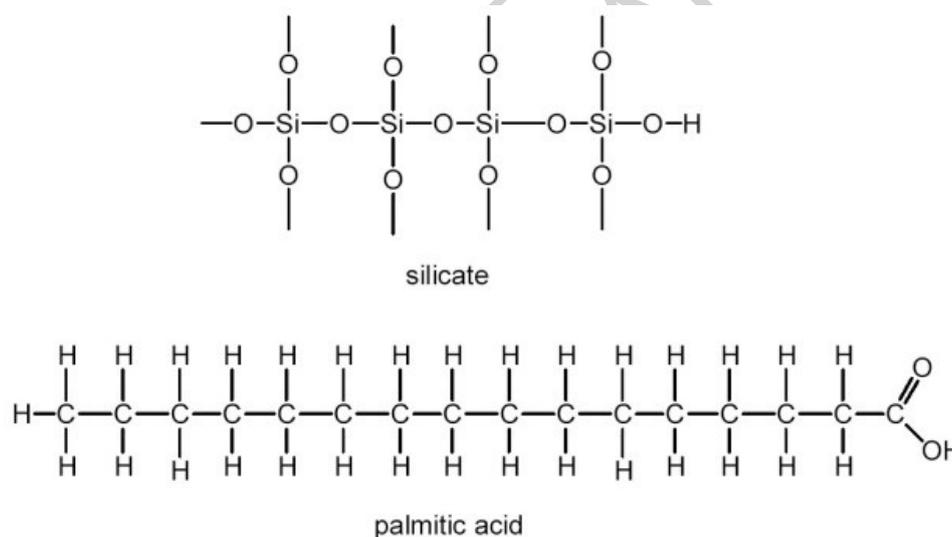


Figure 1: Silicon and carbon atoms are scaffolds that can elongate in four different directions generating four linkages, the two examples refer to the general structure of silicates (the oxygen atoms can be linked to other silicon atoms, for further elongation, or hydrogen atoms)

2.1. The Carbon Atom Building Blocks: Hybridizations

The carbon atom is tetravalent and, as stated before, is a building block that can give rise to four different bonds. These four bonds are oriented in the space at 109.5° , as shown in the first example of Figure 2. However the carbon atom is a very ductile and dynamic building block; it can assume different “hybridizations” that make bonds in

different directions in space. In the so called sp^3 hybridization (first example in Figure 2) the carbon atom generates linkages in four directions at 109.5° exploiting the so defined “orbitals” (spaces that can be occupied by electrons and therefore can generate molecular bonds). Alternatively, in the so called sp^2 hybridization (second example in Figure 2), the carbon atom generates linkages in three directions at 120° . Finally, in the so called sp hybridization (third example in Figure 2), the carbon atom generates linkages in two directions at 180° . It is interesting to note that 109.5° , 120° and 180° are the angles that allow respectively four, three and two linkages to be at the highest reciprocal distance.

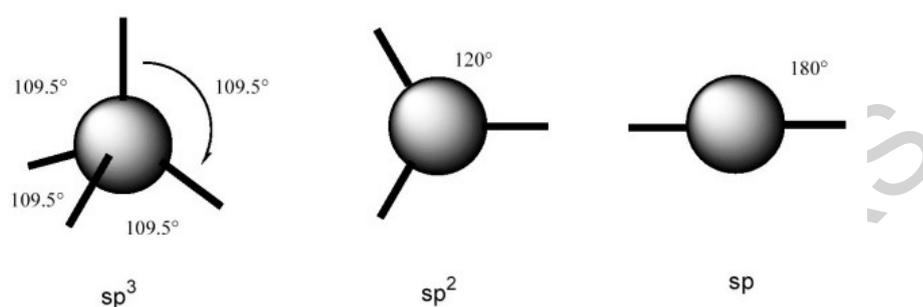


Figure 2: The different hybridization of carbon atom allows it to generate bonds in different directions in space.

2.2. Single and Multiple Bonds

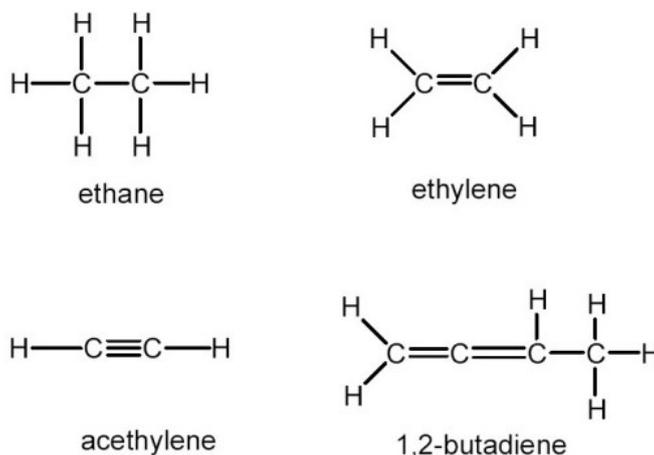


Figure 3: Ethane has two carbon atoms with sp^3 hybridization, which generate four σ -bonds each. Ethylene has two carbon atoms with sp^2 hybridization, generating each three σ -bonds and one π -bond. Acetylene has two carbon atoms with sp hybridization, generating each two σ -bonds and two π -bond. 1,2-Butadiene has one carbon atom hybridized sp , generating one σ -bonds and one π -bond with each of the two carbon atoms linked to it.

The linkages so far described, that join the atoms like a line starting from the centre of each atom, are defined sigma (σ) bonds. Without entering into details on the nature of

the orbitals that generate the molecular bonds, in the sp^2 hybridization the carbon atom will generate also a second bond, defined pi-Greek (π) bond, with one of the three atoms with which it is linked; in other words a double bond is generated (see ethylene in Figure 3). The carbon atom with an sp hybridization will create two more bonds (π bonds) with one of the two atoms linked to him, therefore generating a triple bond (see acetylene in Figure 3). Alternatively, the sp hybridized carbon atom can generate two double bond (see 1,2-butadiene in Figure 3). In each case the carbon atom generates in total four bonds.

The hybridization of the carbon atoms is a dynamic feature, which means that in a chemical reaction a single carbon atom can change the hybridization, and consequently the geometry of the linkages and the type of bounds.

3. Structure of Organic Compounds

Once we know the geometry of the three carbon atom building blocks, we can start to build and represent the organic molecules emphasizing their size and geometry. In order to do that we need a conventional method to draw the three-dimensional structures in two dimensions on a sheet of paper.

3.1. Graphical Representation of the Structures of Organic Compounds

Historically, the first way to represent the structure of organic compounds was simply to draw the four linkages established by a carbon atom with four lines at 90° , linking the neighboring atoms, as in Figure 1 for palmitic acid. This representation is still used, although it does not respect the correct angles of the tetrahedral sp^3 carbon atom (109.5°). However, it is also time consuming for large molecules such as palmitic acid.

The evolution of the methods of graphical representation of organic molecules has followed two different requirements, that of simplicity and the need to give information on the real geometry of the molecule, if required. Therefore, different conventional representations find application depending on what we want to highlight. In order to simplify the representation of an organic compound, the lines representing the bonds can be omitted, like in Figure 4B for a simpler representation of palmitic acid. A further simplification allows us to represent a sequence (chain) of CH_2 with just one CH_2 in brackets, with a subscript number indicating the amount of CH_2 in the chain (Figure 4C). Another way to represent organic molecules, which simplifies the drawing as much as possible, and is therefore useful and often indispensable to represent molecules with very complex structures, omits the symbols of carbon and hydrogen atoms. The molecule is represented with a sequence of lines, as reported in Figure 4D for palmitic acid, each angle and extremity represent a carbon atom linked to the hydrogen needed to complete the structure.

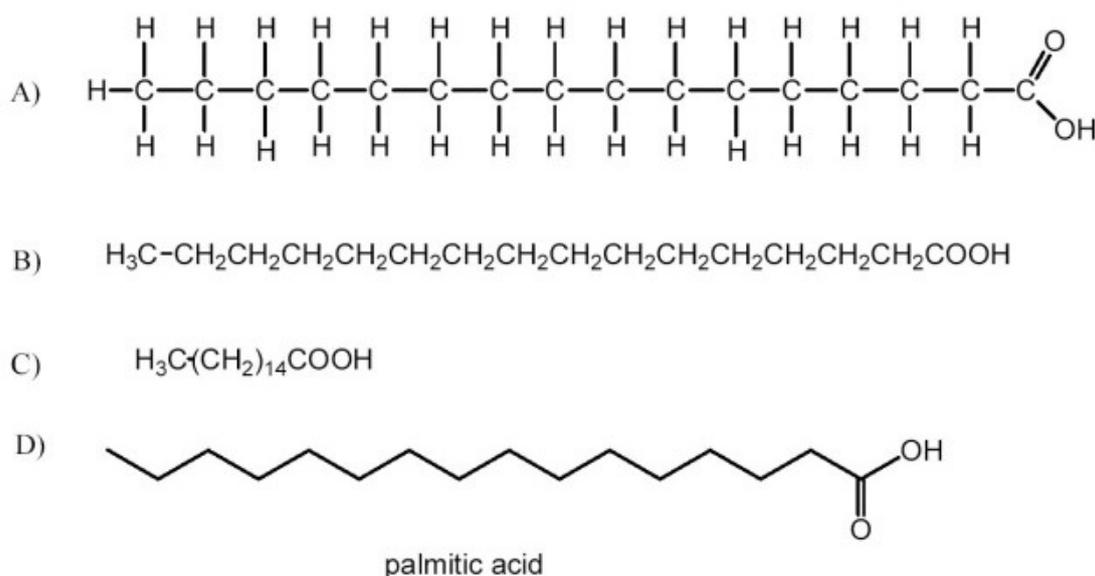


Figure 4: Conventional representations of organic compounds. In A all the bonds and atoms are represented, but the real geometry of the bonds is not respected. In B the bonds are omitted for simplicity; in C the representation of the carbon chain is simplified, in D the symbols of the atoms in the carbon chain are omitted for simplicity.

This last representation can be adopted to show the real geometry of the bonds of a sp^3 hybridized carbon atom, two of which are represented by the two lines on the plane, drawn at about 109.5° . The other two bonds, one of which is directed towards the observer and the other to the back of the plane, can be represented respectively with a wedge and a hatched line (Figure 5). Another representation of a sp^3 hybridized carbon atom, which describes the geometry of the bonds, is the historical conventional method invented by Emil Fisher and still used for amino acids and sugars. In the Fisher representation the four bonds are drawn like a cross, with the carbon atom in the centre. The horizontal lines are conventionally oriented towards the observer (out from the plane), whereas the vertical lines are conventionally oriented back to the plane, opposite to the observer (Figure 5, right).

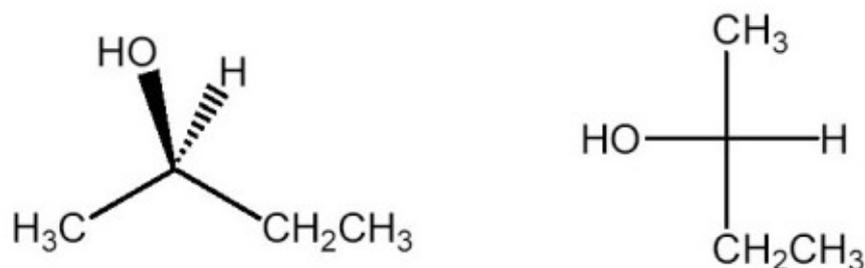


Figure 5: Conventional representations of the sp^3 hybridized carbon atom, describing the real geometry of the molecule.

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The bibliography on Organic Chemistry is extremely wide, and most of the text books are clear and exhaustive. Some books with different characteristics are reported as examples.

Biographical Sketch

Francesco Nicotra was born in Catania in 1950. He graduated in Chemistry at the University of Catania in 1973; then he moved to the University of Milano where he became permanent researcher in 1981 and associated professor in 1987. In 1985 he spent a post-doc period at the University of Orleans, under the supervision of Pierre Sinay. Actually he is full professor of organic chemistry at the University of Milano Bicocca and Director of the Department of Biotechnology and Biosciences. He is member of the IUPAC Committee of Organic and Biomolecular Chemistry and chairman of the subcommittee of Biotechnology. He is also the Italian representative in the International Carbohydrate Organisation. The research interests range across the synthesis of various biologically active compounds, in particular carbohydrates and structural analogs, the development of new synthetic methods and the use of biocatalysis.