A SELF-STUDY GUIDE TO THE PRINCIPLES OF ORGANIC CHEMISTRY

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Key Concepts, Reaction Mechanisms, and Practice Questions for the Beginner

JIBEN ROY

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A Self-Study Guide to the Principles of Organic Chemistry:
Key Concepts, Reaction Mechanisms, and Practice Questions for the Beginner

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To 4 W & 1M

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Not all of them are organic chemists, but all have a common bonding through organic chemistry.

Contents

To the students taking the course of Organic Chemistry

You don't have to be brilliant to survive organic chemistry, but you have to be willing to work at it.

Preface

This book, *A Self-Study Guide to the Principles of Organic Chemistry: Key Concepts, Reaction Mechanisms, and Practice Questions for the Beginner* is written in plain and simple language and it is formatted as a self-study guidebook for the students. For instructors, it is a handbook dealing with all the concepts necessary to understand organic chemistry. It may not be a comprehensive organic chemistry textbook, and certainly it is not going to replace the existing comprehensive organic chemistry textbook, but it has all the elements to build the student's skill and foundation in understanding as well as learning organic chemistry. This book can be considered as the 21st century 'Rosetta Stone,' used to study this foreign language, organic chemistry. By studying this book, students struggling with organic chemistry will be able to grasp the key concepts easily.

Some students taking organic chemistry are very scared of the class, but this central science subject is a requirement for chemistry majors, biology majors or many more related majors. It is intended for both 2 year and 4 year colleges.

Starting with a definition, the book explains atoms, electronic configuration, bonding, hydrocabons, polar reaction mechanism, stereochemistry, reaction varieties, organic spectroscopy, aromaticity and aromatic reactions, essential organic functionalities and their reactions, biomolecules, organic polymers, and a synthetic approach to organic compounds. It emphasizes visual conception through the use of structural drawings and mechanisms, with less narrative so that the student can better visualize the principles of organic chemistry. Students will discover how logical organic chemistry is, and they will certainly need less memorization practicing with pen and paper. Each chapter ends with frequently asked questions and answers, followed by additional practice problems with the answers at the back. The questions and answers section of each chapter is an integral part of the formulae for understanding organic chemistry. Almost all the most essential concepts in organic chemistry are introduced in a systematic manner so that the students find them logical, easier, and challenging as well.

I am really happy to have found a person like Jeff Young who has built up a publishing company based on publishing unique books at a lower cost while taking care of a worthy manuscript from A to Z. I am thankful to Jeff for selecting and taking care of my book in publication and distribution to the students around the world. I am also indebted to the production editor of my book, Christie Mayer, and cover designer, Shereen Siddiqui, who each did an excellent job on the book.

I am thankful to my organic chemistry students, especially the class of Fall 2012, who have used part of the manuscript and found it effective in their understanding. I am grateful to my colleagues Dr. Dionne Fortenberry, Dr. Ghanshyam Heda, and friends and well-wishers for their encouragement. Finally, I would appreciate hearing from the students and instructors about the book and its improvement for the future.

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About the Author

Dr. Jiben Roy is a professor of chemistry in the Department of Sciences and Mathematics, Mississippi University for Women. He earned his Ph.D. in organic chemistry from the University of Saskatchewan, Canada in 1983, and went on to complete his post-doctoral fellowship at the Hawaii Natural Energy Institute, University of Hawaii at Manoa 1984-1985. Dr. Roy has established an impressive track record in teaching and research, while also working in the pharmaceutical industry with bulk drugs and formulations, both in the United States and abroad. His publications include *An Introduction to Pharmaceutical Sciences: Production, Chemistry, Techniques & Technology* (2011), *Organic Chemistry* (in Bengali) (1979), over four dozen other publications, and a co-edited special issue of the journal *Current Medicinal Chemistry*.

1 Introduction to Organic Chemistry

Key Concept Terms

Definition of organic chemistry	Commonly used elements in organic compounds
Electronic configuration of organic elements	Importances of organic compounds
Environmental hazards of some organic compounds	Reasons for millions of organic compounds

1.1 Definition of Organic Chemistry

Sugar, gasoline, peanut butter, plastics, aspirin, paper, milk, cotton, wood, meat, apples, spinach, beer and most of the substances important to life and life styles have one thing common: they all contain the element **CARBON (C)**. Carbon is such a unique and important element that an entire branch of chemistry studying carbon and its compounds is known as organic chemistry. Organic chemistry is thus the study of the chemistry of carbon containing compounds. Several millions of such compounds are currently known. A more appropriate definition of organic chemistry is: **The chemistry of hydrocarbons (compounds of carbon and hydrogen only) and the derivatives of hydrocarbons, (compounds containing C, H, and O, N, S, P, halogens etc).** In some organic compounds, the metals such as Na, K, Ca and many others can be found. These compounds are called organo-metallic compounds.

However, there are some exceptions: carbonates (CO_3^{-2}), bicarbonates (HCO_3^{-1}), cyanides (CN^{-1}) of metals, CS_2 and a few gases such as CO, CO_2, HCN etc., are not considered organic compounds. Thus, they are treated in Inorganic Chemistry. However, the compounds containing carbon and hydrogen, i.e. hydrocarbons, are always considered organic compounds. This is the foundation of organic chemistry. The derivatives of hydrocarbon, i.e., the compounds derived from hydrocarbon by replacing one or more atoms of hydrogen, form the vast majority of organic compounds **(Figure 1.1)**.

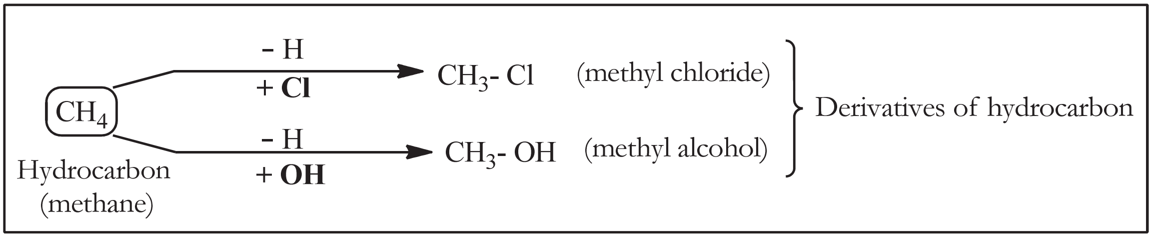


Figure 1.1 Hydrocarbon, methane and its derivatives

The Periodic Table contains more than one hundred elements; however, organic chemistry deals mostly with **only certain elements**. The partial Periodic Table is shown below **(Figure 1.2)**, where the elements involved in organic compounds are shown in black.

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	Kr 36
5																	53 I	54 Xe

Figure 1.2 The Partial Periodic Table where the elements mostly involved in Organic Compounds are shown in black shade. Group 1= Alkali metals (except H); Group 2= Alkaline earth metals; Group 17=Halogens; Group 18=Inert or noble gas

1.2 Electron Configuration of the Elements Commonly Involved in Organic Compounds

It is thus very important to know the properties of these elements involved in organic compounds **(Table 1.1)**. The electronic configuration of these elements would help to understand the structure of organic compounds. Most of the elements are non-metal, except Li, Na, Mg, K, and Ca, which are the metals that form organo-metallic compounds, as previously mentioned. Information on isotopes of these elements involved in organic compounds is also included. Isotopes have same atomic number (number of protons) but a different mass number (number of neutrons). Examples: Hydrogen with

Mass number 1(no neutron) has two more isotopes, deuterium with mass number 2 (1 neutron) and tritium with mass number 3 (2 neutrons). Similarly carbon has ^{12}C which is almost 99% available naturally with two other isotopes, ^{13}C and ^{14}C.

Table 1.1 Fact Sheet of most common elements in Organic Compounds

Name of element (Symbol)	Group (Period)	Block	At. No. (At. mass)	Physical State	Electron Configuration	Isotopes
Hydrogen (H)	1 (1)	s	1 (1)	Gas(H_2)	$1s^1$	^1H,^2H, ^3H
Lithium (Li)	1 (2)	s	3 (7)	Solid	$1s^22s^1$ or [He]$2s^1$	^7Li, ^6Li
Carbon (C)	14 (2)	p	6 (12)	Solid	$1s^22s^22p^2$ or $1s^22s^22p_x^12p_y^12p_z^0$ or [He]$2s^22p^2$	^{12}C,^{13}C, ^{14}C
Nitrogen (N)	15 (2)	p	7 (14)	Gas(N_2)	$1s^22s^22p^3$ or $1s^22s^22p_x^12p_y^12p_z^1$ or [He]$2s^22p^3$	^{14}N
Oxygen (O)	16 (2)	p	8 (16)	Gas(O_2)	$1s^22s^22p^4$ or $1s^22s^22p_x^22p_y^12p_z^1$ or [He]$2s^22p^4$	^{16}O, ^{18}O
Fluorine (F)	17 (2)	p	9 (19)	Gas(F_2)	$1s^22s^22p^5$ or $1s^22s^22p_x^22p_y^22p_z^1$ or [He]$2s^22p^5$	^{19}F
Sodium (Na)	1 (3)	s	11 (23)	Solid	$1s^22s^22p^63s^1$ or [Ne]$3s^1$	^{23}Na
Magnesium (Mg)	2 (3)	s	12 (24)	Solid	$1s^22s^22p^63s^2$ or [Ne]$3s^2$	^{24}Mg,^{25}Mg, ^{26}Mg
Phosphorus (P)	15 (3)	p	15 (31)	Solid	$1s^22s^22p^63s^23p^3$ or [Ne] $3s^23p^3$	^{31}P
Sulfur (S)	16 (3)	p	16 (32)	Solid	$1s^22s^22p^63s^23p^4$ or [Ne] $3s^23p^4$	^{32}S
Chlorine (Cl)	17 (3)	p	17 (35.5)	Gas (Cl_2)	$1s^22s^22p^63s^23p^5$ or [Ne] $3s^23p^5$	^{35}Cl, ^{37}Cl
Potassium (K)	1 (4)	s	19 (39)	Solid	$1s^22s^22p^63s^23p^64s^1$ or [Ar]$4s^1$	^{39}K
Calcium (Ca)	2 (4)	s	20 (40)	Solid	$1s^22s^22p^63s^23p^64s^2$ or [Ar]$4s^2$	^{40}Ca
Bromine (Br)	17 (4)	p	35 (80)	Liquid (Br_2)	$1s^22s^22p^63s^23p^63d^{10}4s^24p^5$ or [Ar] $3d^{10}4s^24p^5$	^{79}Br, ^{81}Br
Iodine (I)	17 (5)	p	53 (127)	Solid (I_2)	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$-$4d^{10}5s^25p^5$ or [Kr] $4d^{10}5s^25p^5$	^{127}I

The building up (Aufbau Principle) of electron configuration with the increase of atomic number (similar increase in number of electrons) depends on the energy levels of orbitals. Orbital energy levels are shown in **Figure 1.3.** You can see 1s orbital has the lowest energy, then 2s, followed by 2p orbitals. The 2p orbitals consist of 3 degenerate orbitals.

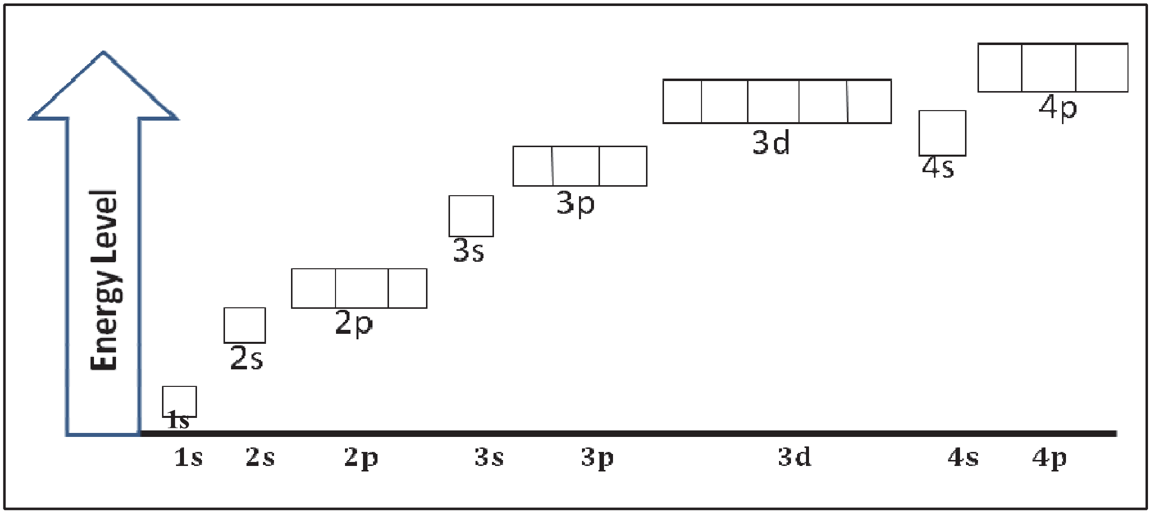


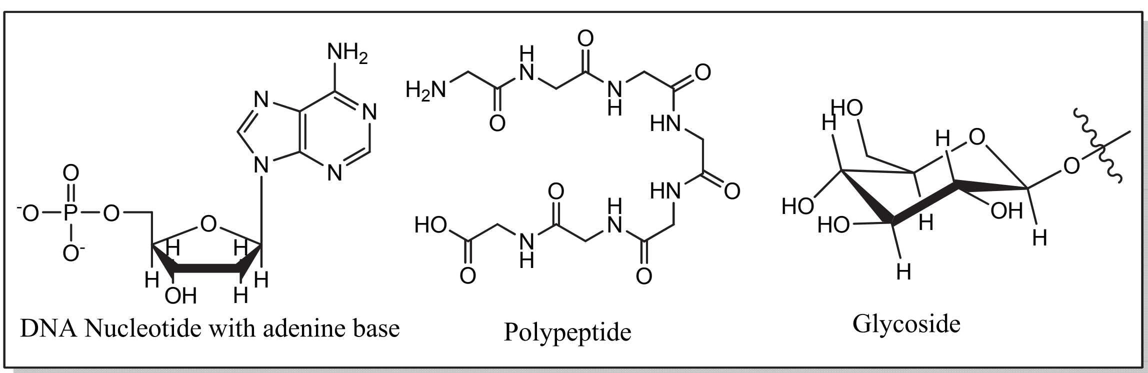
Figure 1.3 The Orbital Energy Diagram

1.3 Occurrences, Importance and Hazards of Organic Compounds

Organic chemistry is a versatile discipline of sciences. The human body is made up of organic compounds. We synthesize organic compounds and we also eat organic compounds. We have industry based on organic compounds. A few examples are shown below:

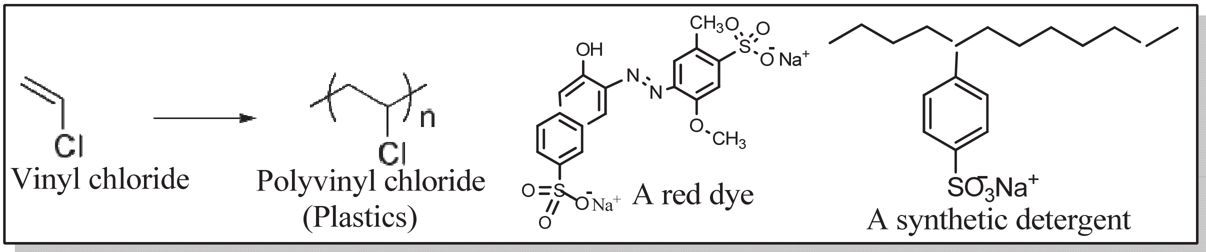
[a] Living organisms: Living organisms ingest organic compounds and convert it into almost all of the compounds necessary for life.

Food ⟹ DNA, amino acids, polypeptides, proteins, enzymes, fats, glycosides, etc.



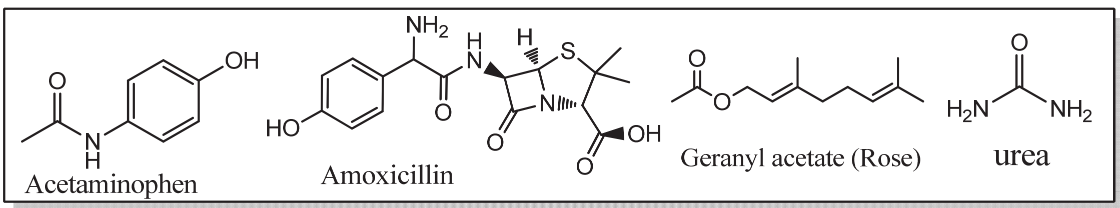
[b] Industrial Organic Compounds: Carbon containing substances are converted into useful products.

Coal, oil, natural gas ⇒ plastics, fibres, dyes, detergents, solvents, chemical building blocks

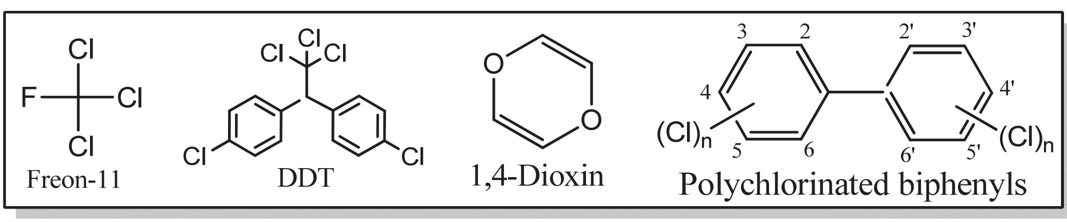


[c] Fine Chemical Industry: Complex molecules are synthesized from simpler ones.

Simpler carbon compounds ⇒ Pharmaceuticals, agrochemicals, Cosmetics



[d] Environmental hazards: Industrial processes have produced a number of environmentally dangerous organic compounds, including Freon (destroys ozone layer), pesticides, (DDT), dioxin, PCB, and abused drugs.



[e] Branches of Science Based on Organic Chemistry: Biotechnology, microbiology, biochemistry, pharmacy, medical sciences, agriculture.

At a glance, these applications of organic chemistry (organic compounds) can be seen in **Figure 1.4.**

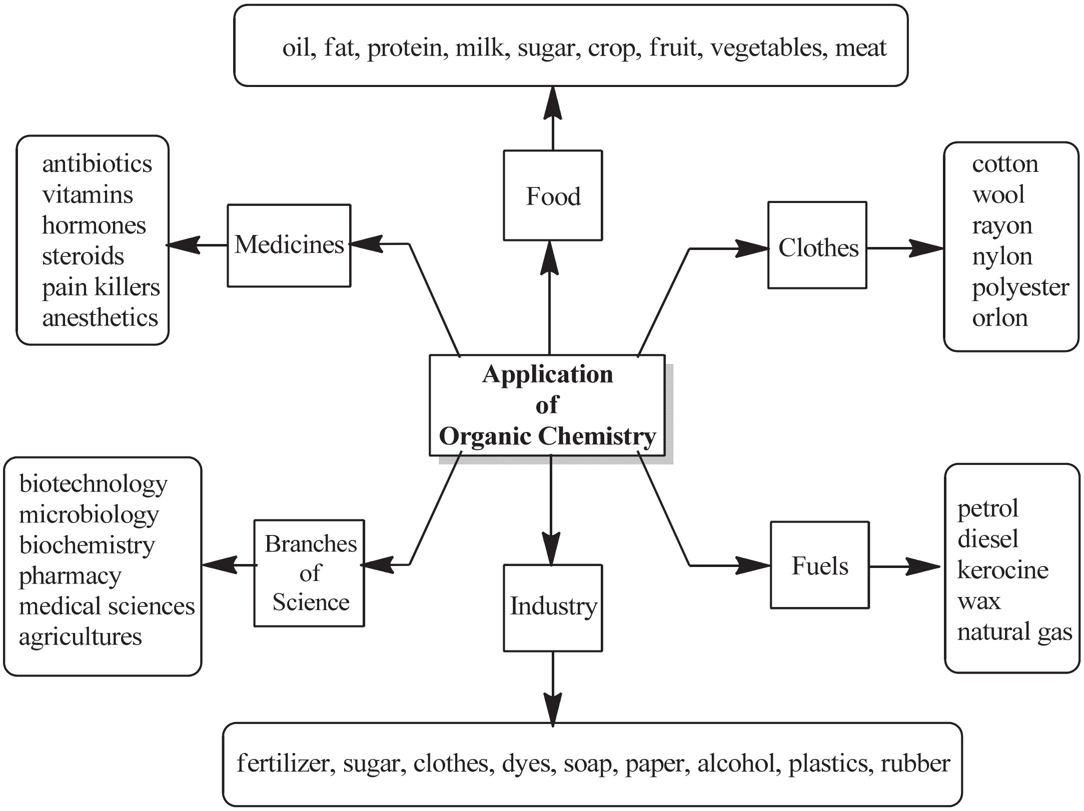
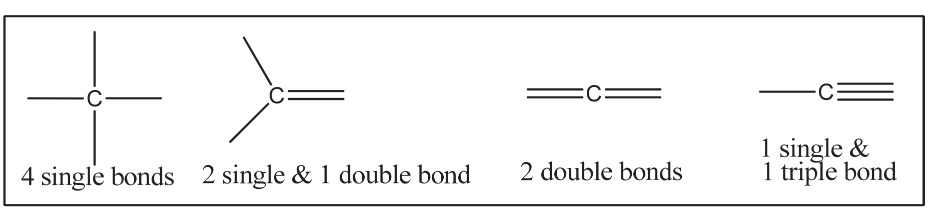


Figure 1.4 Application of organic chemistry

1.4 Why are there Millions of Organic Compounds (Carbon Containing Compounds)?

There are number of characteristics of carbon and carbon compounds which can explain the formation of millions of organic compounds. The number of organic compounds is increasing every day.

[1] Carbon forms 4 covalent bonds with other non-metal atoms and these 4 bonds can be formed in different ways.



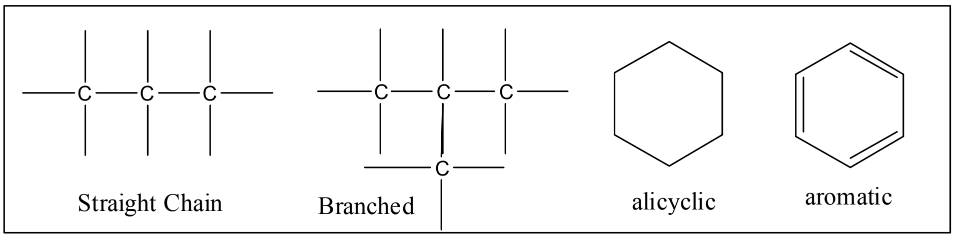
[2] Carbon also forms organometallic compounds containing carbon – metal bonds.

$\overset{\delta-}{C}$ — $\overset{\delta+}{M}$ **(Highly polar, covalent Organocmetallic compounds)**

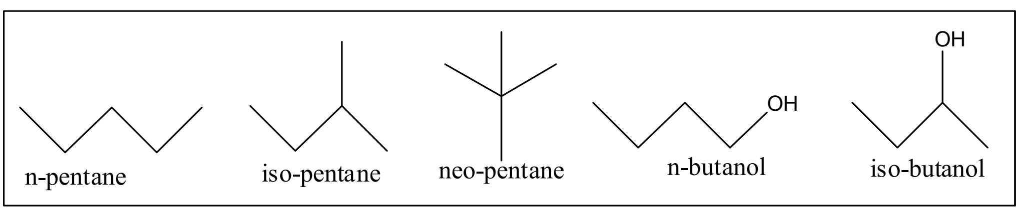
H_3C - Li : Methyl Litium R - MgX : Alkyl magnesium halide (Grignard reagent)

$(CH_3)_2\ Cu^-\ Li^+$: Lithium dialkyl Copper (Gilman reagent)

[3] Carbon to carbon bond formations, also known as catenation, can be formed in many different ways: straight, branching or alicyclic and aromatic.



[4] Isomerism – the same molecular formula but in a different structure can lead to many different compounds, for example pentane can have two more isomers. Similarly, decane can have a total of 75 isomers. Hydrocarbon derivatives also rearrange to produce isomers, such as n-butanol and isobutanol.



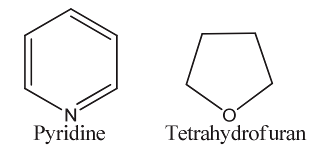
[5] Functional group derivatives of carbon – using just 2 carbon chains could lead to many derivatives. A few derivatives are shown below.

CH_3CH_2-OH	CH_3-COOH	CH_3-CHO	CH_3CH_2-NH_2	CH_3-O-CH_3
Alcohol	Acid	Aldehyde	Amine	Ether

[6] Organic acids form ionic compounds with metals to form salts.

CH_3CH_2-COO^-Na^+ (sodium propionate)	($^-$OOC- COO$^-$) Ca^{2+} (calcium oxalate)

[7] Formation of heterocyclic compounds- if there is 1 or 2 atoms other than carbon in the ring, heterocyclic compounds are formed.



1.5 Frequently Asked Questions & Answers

1] Write an electron configuration of ground and excited state of carbon atom.

Answer

Carbon has 6 electrons, which has the following electron configuration:
(Ground state) C(6) = $1s^22s^22p^2$ or $1s^22s^22p_x^12p_y^12p_z^0$ or $1s^22s^22p_x^12p_y^1$ or [He]$2s^22p^2$
(Excited state) $C^*(6)$ = $1s^22s^12p_x^12p_y^12p_z^1$ or [He]$2s^12p_x^12p_y^12p_z^1$

2] What would be electron configuration of Na^+ and Cl^-?

Answer

Sodium (Na) has 11 electrons and in Na^+ ion, there is 1 less electron than Na. However, Cl^- will have 1 more electron compared to Cl (17 electrons).

Na(11) = $1s^22s^22p^63s^1$ or [Ne]$3s^1$
Na^+(10) = $1s^22s^22p^6$ or [Ne]

Cl(17) = $1s^22s^22p^63s^23p^5$ or [Ne] $3s^23p^5$
Cl^-(18) = $1s^22s^22p^63s^23p^6$ or [Ar]

3] Name an organic compound containing phosphorous or sulfur.

Answer

Most important example of P-containing organic compound is DNA (Deoxyribonucleic acid), which is a polymer and its monomer is nucleotide. Similar to alcohol, there is thiol, such as CH_3CH_2-SH.

4] [Multiple choice question] Which one is not an organic compound?

(a) sucrose (b) splenda (c) cooking gas (d) baking soda (e) PVC

Answer

Correct is (d) baking soda ($NaHCO_3$)

1.6 Additional Practice Questions (Answers at the back)

5] Draw all the possible isomers of hexane.

6] What are the isotopes of chlorine? Include their natural abundance.

7] How many electrons 2p, 3p and 3d orbitals can accommodate?

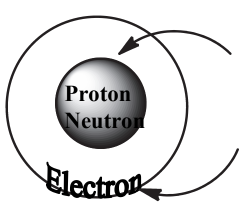
2 Atoms, Bonding, Orbitals, Hybridization, Polarity, and Electronegativity

Key Concept Terms

Atom	Bond formation	Electrons distribution around nucleus	Valence electron
Lewis dot formula	Hybridization sp^3, sp^2, sp	π bond and σ bond	Covalent bond
Polarity	Electronegativity	Inductive effect	Dipole moment	Formal charge

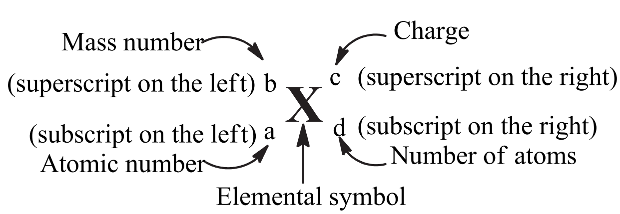
2.1 Atoms

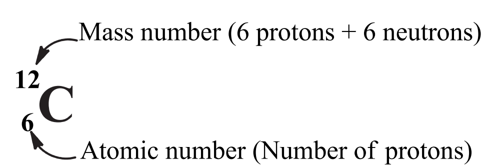
An atom is the smallest fundamental unit of an element. It is made up of nucleus surrounded by orbiting electron(s). The proton and neutron in the nucleus at the center of atom are fixed; however, electron(s) is(are) always in motion. The positively charged nucleus is attracted by the moving negatively charged electron.



Nucleus : consists of proton (positively charged) and neuton (neutral). Hydrogen atom is only exception where there is only proton & **no** neutron.
Negatively charged electrons

Figure 2.1 Atomic Structure





2.2 Bond Formation and Arrangement of Electrons

When one atom comes close to another atom, a bond is formed. A pair of electrons through sharing makes a bond (covalent bonding). Or the bond may be formed by the transfer of electrons making positive and negatively charged ions (ionic). The question is electrons are negatively charged, so when they come closer, there should be repulsion. In that case, how is a bond formed?

In fact, positively charged nucleus of one atom is also attracted by the negatively electron of the other atom and vice versa (Figure 2.2).

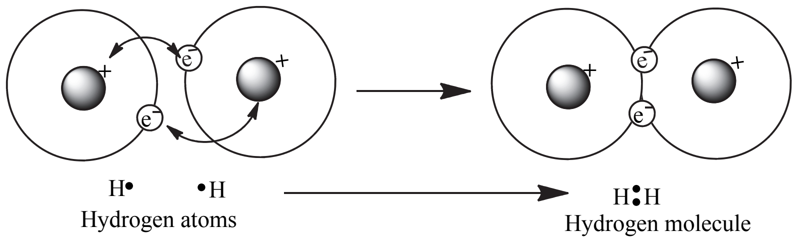


Figure 2.2 Formation of bond between two hydrogen atoms

To understand bonding, we need to refresh our memory with the arrangement of electrons around the nucleus of an atom. The electrons are distributed in different orbitals (sub-energy levels), which are housed in different orbit or shells (energy levels). The arrangement of electrons around the nucleus is summarized in Figure 2.3. It is important to remember that it is only valence electrons that can participate in bonding. In addition, during the formation of covalent bonds in organic compounds, the unpaired electrons make bonds.

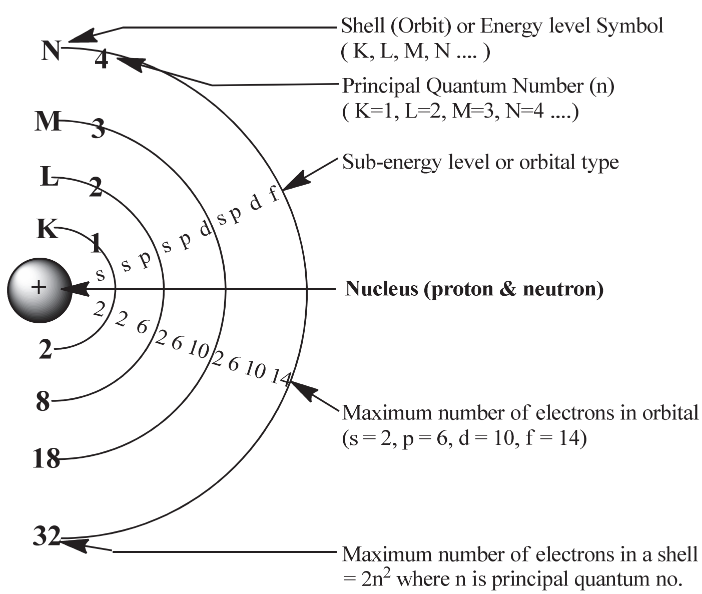


Figure 2.3 Arrangement of electrons around the nucleus

2.3 Valance Electrons

Valence electrons are those that inhabit the outermost shells, energy levels, or highest principal quantum number. These electrons participate in making bonds. On the other hand, the electrons in the inner shells, which do not participate in making bonds, are called **core electrons**. From the electron configuration, both core and valence electrons can be determined. The number of valence electrons and number of possible bonds are shown in Table 2.1.

Table 2.1 Determination of valence electrons based on electron configuration

Name of element (Symbol)	At. No	Electron Configuration (Valence electrons are in bold)	Block	No. of Core electrons	Number of Valence electrons	Number of possible bonds
Hydrogen (H)	1	$\mathbf{1s^1}$	s	0	1	1
Carbon (C)	6	$1s^2\mathbf{2s^22p^2}$ or $1s^2\mathbf{2s^22p_x^12p_y^12p_z^0}$ or $[He]\mathbf{2s^22p^2}$	p	2	4	4
Nitrogen (N)	7	$1s^2\mathbf{2s^22p^3}$ or $1s^2\mathbf{2s^22p_x^12p_y^12p_z^1}$ or $[He]\mathbf{2s^22p^3}$	p	2	5	3
Oxygen (O)	8	$1s^2\mathbf{2s^22p^4}$ or $1s^2\mathbf{2s^22p_x^22p_y^12p_z^1}$ or $[He]\mathbf{2s^22p^4}$	p	2	6	2
Fluorine (F)	9	$1s^2\mathbf{2s^22p^5}$ or $1s^2\mathbf{2s^22p_x^22p_y^22p_z^1}$ or $[He]\mathbf{2s^22p^5}$	p	2	7	1
Sodium (Na)	11	$1s^22s^22p^6\mathbf{3s^1}$ or $[Ne]\mathbf{3s^1}$	s	10	1	1
Phosphorus (P)	15	$1s^22s^22p^6\mathbf{3s^23p^3}$ or $[Ne]\ \mathbf{3s^23p^3}$	p	10	5	3 or 5
Sulfur (S)	16	$1s^22s^22p^6\mathbf{3s^23p^4}$ or $[Ne]\ \mathbf{3s^23p^4}$	p	10	6	2
Chlorine (Cl)	17	$1s^22s^22p^6\mathbf{3s^23p^5}$ or $[Ne]\ \mathbf{3s^23p^5}$	p	10	7	1
Potassium (K)	19	$1s^22s^22p^63s^23p^6\mathbf{4s^1}$ or $[Ar]\mathbf{4s^1}$	s	18	1	1
Calcium (Ca)	20	$1s^22s^22p^63s^23p^6\mathbf{4s^2}$ or $[Ar]\mathbf{4s^2}$	s	18	2	2
Bromine (Br)	35	$1s^22s^22p^63s^23p^63d^{10}\mathbf{4s^24p^5}$ or $[Ar]\ 3d^{10}\mathbf{4s^24p^5}$	p	28	7	1
Iodine (I)	53	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}\mathbf{5s^25p^5}$ or $[Kr]\ 4d^{10}\mathbf{5s^25p^5}$	p	46	7	1