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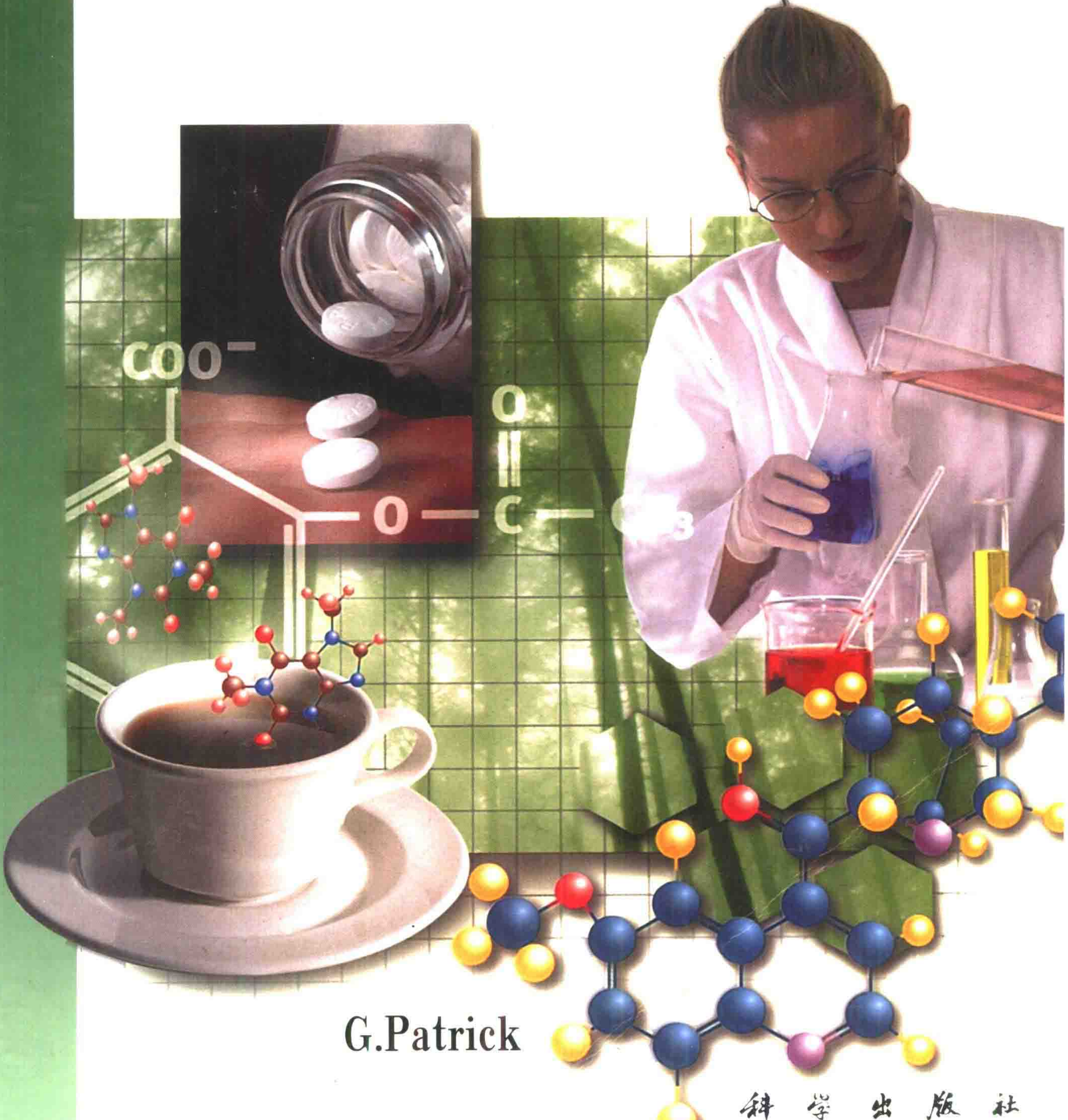
ORGANIC CHEMISTRY

有机化学



G.Patrick

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（影印版）

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内容简介

本书是国外优秀教材畅销榜的上榜教材，面向大学本科生，由英国著名大学具有丰富教学经验的一流教授编写，它以一种风格独特的方式，全面、系统地概括了有机化学的核心内容和前沿动态，并以一种便于学习、利于复习的编写形式，使学生能快速、准确的掌握知识，很好地指导学习和考试。本书配有全新绘制和编写的插图与表格，非常有指导性，是其他教材无法比拟的。本书的简明和扼要也为大学教师备课提供了最好的参考。书中英文使用最为自然、易懂的语句，是提高专业外语的最佳用书。

G. L. Patrick
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PREFACE

This textbook aims to provide a comprehensive set of basic notes in organic chemistry, which will be suitable for undergraduate students taking chemistry, chemistry-related courses, or courses which involve organic chemistry as an ancillary subject. The book concentrates on core topics which are most likely to be common to those organic chemistry courses which follow on from a foundation or introductory general chemistry course.

Organic chemistry is a subject which can lead some students to the heights of ecstasy, yet drive others up the wall. Some students 'switch on' to it immediately, while others can make neither head nor tail of it, no matter how hard they try. Certainly, one of the major problems in studying the subject is the vast amount of material which often has to be covered. Many students blanche at the prospect of having to learn a seemingly endless number of reactions, and when it comes to drawing mechanisms and curly arrows, they see only a confusing maze of squiggly lines going everywhere yet nowhere. The concepts or organic reaction mechanisms are often the most difficult to master. These difficulties are often compounded by the fact that current textbooks in organic chemistry are typically over 1200 pages long and can be quite expensive to buy.

This book attempts to condense the essentials of organic chemistry into a manageable text of 310 pages which is student friendly and which does not cost an arm and a leg. It does this by concentrating purely on the basics of the subject without going into exhaustive detail or repetitive examples. Furthermore, key notes at the start of each topic summarize the essential facts covered and help focus the mind on the essentials.

Organic chemistry is a peculiar subject in that it becomes easier as you go along! This might seem an outrageous statement to make, especially to a first-year student who is struggling to come to terms with the rules of nomenclature, trying to memorize a couple of dozen reactions and making sense of mechanisms at the same time. However, these topics are the basics of the subject and once they have been grasped, the overall picture becomes clear.

Understanding the mechanism of how a reaction takes place is particularly crucial in this. It brings a logic to the reactions of the different functional groups. This in turn transforms a list of apparently unrelated fats into a sensible theme which makes remembering the reactions a 'piece of cake' (well, nearly).

Once this happy state of affairs has been reached, the relevance of organic chemistry to other subjects such as genetics and biochemistry suddenly leaps off the page. Understanding organic chemistry leads to a better understanding of life chemistry and how the body works at the molecular level. It also helps in the understanding of the molecular mechanisms involved in disease and bodily malfunction, leading in turn to an understanding of how drugs can be designed to cure these disease states – the science of medicinal chemistry.

And that's not all. An understanding of organic chemistry will help the industrial chemist or chemical engineer faced with unexpected side-reactions in a chemical process, and the agro-scientist trying to understand the molecular processes taking place within plants and crops; and it will assist in the design and synthesis of new herbicides and fungicides which will be eco-friendly. It

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will aid the forensic scientist wishing to analyze a nondescript white powder – is it heroin or flour?

The list of scientific subject areas involving organic chemistry is endless – designing spacesuits, developing new photographic dyes, inventing new molecular technology in microelectronics – one could go on and on. Organic chemistry is an exciting subject since it leads to an essential understanding of molecules and their properties.

The order in which the early topics of this book are presented is important. The first two sections cover structure and bonding, which are crucial to later sections. Just why does carbon form four bonds? What is hybridization?

The third section on functional groups is equally crucial if students are to be capable of categorizing the apparent maze of reactions which organic compounds can undergo. It is followed by stereochemistry, sections E and F, in which the basic theory of reactions and mechanisms is covered. What are nucleophiles and electrophiles? What does a mechanism represent? What does a curly arrow mean?

The remaining sections can be used in any order and look at the reactions and mechanisms of the common functional groups which are important in chemistry and biochemistry.

It is hoped that students will find this textbook useful in their studies and that once they have grasped what organic chemistry is all about they will read more widely and enter a truly exciting world of molecular science.

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A1 ATOMIC STRUCTURE OF CARBON

Key Notes

Atomic orbitals	The atomic orbitals available for the six electrons of carbon are the s orbital in the first shell, the s orbital in the second shell and the three p orbitals in the second shell. The $1s$ and $2s$ orbitals are spherical in shape. The $2p$ orbitals are dumbbell in shape and can be assigned $2p_x$, $2p_y$ or $2p_z$ depending on the axis along which they are aligned.
Energy levels	The $1s$ orbital has a lower energy than the $2s$ orbital which has a lower energy than the $2p$ orbitals. The $2p$ orbitals have equal energy (i.e. degenerate).
Electronic configuration	Carbon is in the second row of the periodic table and has six electrons which will fill up lower energy atomic orbitals before entering higher energy orbitals (aufbau principle). Each orbital is allowed a maximum of two electrons of opposite spin (Pauli exclusion principle). When orbitals of equal energy are available, electrons will occupy separate orbitals before pairing up (Hund's rule). Thus, the electronic configuration of a carbon atom is $1s^2$ $2s^2$ $2p_x^1$ $2p_y^1$.
Related topic	Covalent bonding and hybridization (A2)

Atomic orbitals

Carbon has six electrons and is in row 2 of the periodic table. This means that there are two shells of atomic orbitals available for these electrons. The first shell closest to the nucleus has a single s orbital – the $1s$ orbital. The second shell has a single s orbital (the $2s$ orbital) and three p orbitals ($3 \times 2p$). Therefore, there are a total of five atomic orbitals into which these six electrons can fit. The s orbitals are spherical in shape with the $2s$ orbital being much larger then the $1s$ orbital. The p orbitals are dumbbell-shaped and are aligned along the x, y and z axes. Therefore, they are assigned the $2p_x$, $2p_y$ and $2p_z$ atomic orbitals (*Fig. 1*).

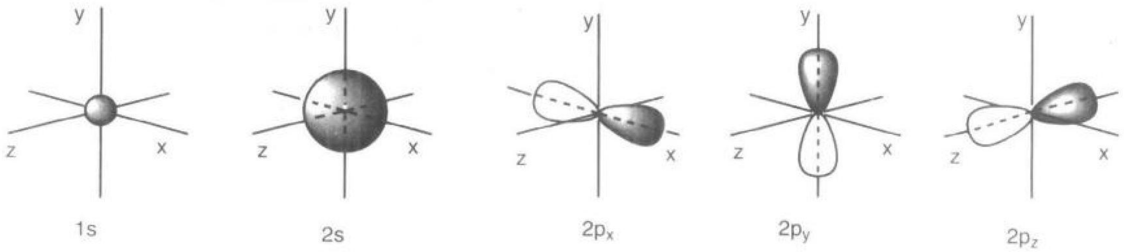

Fig. 1. Atomic orbitals.

Energy levels

The atomic orbitals described above are not of equal energy (*Fig. 2*). The 1*s* orbital has the lowest energy. The 2*s* orbital is next in energy and the 2*p* orbitals have the highest energies. The three 2*p* orbitals have the same energy, meaning that they are **degenerate**.

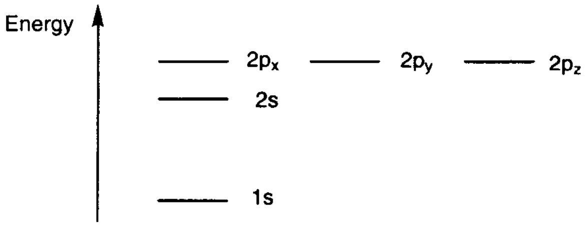

Fig. 2. Energy levels of atomic orbitals.

Electronic configuration

Carbon is in the second row of the periodic table and has six electrons which will fill up the lower energy atomic orbitals first. This is known as the **aufbau principle**. The 1*s* orbital is filled up before the 2*s* orbital, which is filled up before the 2*p* orbitals. The **Pauli exclusion principle** states that each orbital is allowed a maximum of two electrons and that these electrons must have opposite spins. Therefore, the first four electrons fill up the 1*s* and 2*s* orbitals. The electrons in each orbital have opposite spins and this is represented in *Fig*. 3 by drawing the arrows pointing up or down. There are two electrons left to fit into the remaining 2*p* orbitals. These go into separate orbitals such that there are two half-filled orbitals and one empty orbital. Whenever there are orbitals of equal energy, electrons will only start to pair up once all the degenerate orbitals are half filled. This is known as **Hund's rule**.

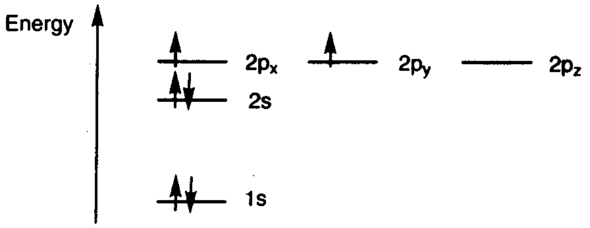

Fig. 3. Electronic configuration for carbon.

The electronic configuration for carbon is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$. The numbers in superscript refer to the numbers of electrons in each orbital. The letters refer to the types of atomic orbital involved and the numbers in front refer to which shell the orbital belongs.

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A2 COVALENT BONDING AND HYBRIDIZATION

Key Notes

Covalent bonding	When two hydrogen atoms approach each other, their 1*s* atomic orbitals interact to form a bonding and an antibonding molecular orbital (MO). A stable covalent bond is formed when the bonding MO is filled with a pair of electrons and the antibonding MO is empty.
Sigma bonds	Sigma (σ) bonds are strong bonds with a circular cross-section formed by the head-on overlap of two atomic orbitals.
Hybridization	The electronic configuration of atomic carbon implies that carbon should form two bonds. However, it is known that carbon forms four bonds. When carbon is part of an organic structure, it can 'mix' the 2*s* and 2*p* orbitals of the valence shell in a process known as hybridization. There are three possible types of hybridization – sp^3, sp^2 and *sp* hybridization.
Related topics	Atomic structure of carbon (A1) sp^3 Hybridization (A3) sp^2 Hybridization (A4) *sp* Hybridization (A5)

Covalent bonding A covalent bond binds two atoms together in a molecular structure and is formed when atomic orbitals overlap to produce a **molecular orbital** – so called because the orbital belongs to the molecule as a whole rather than to one specific atom. A simple example is the formation of a hydrogen molecule (H_2) from two hydrogen atoms. Each hydrogen atom has a half-filled 1*s* atomic orbital and when the atoms approach each other, the atomic orbitals interact to produce two MOs (the number of resulting MOs must equal the number of original atomic orbitals, *Fig. 1*).

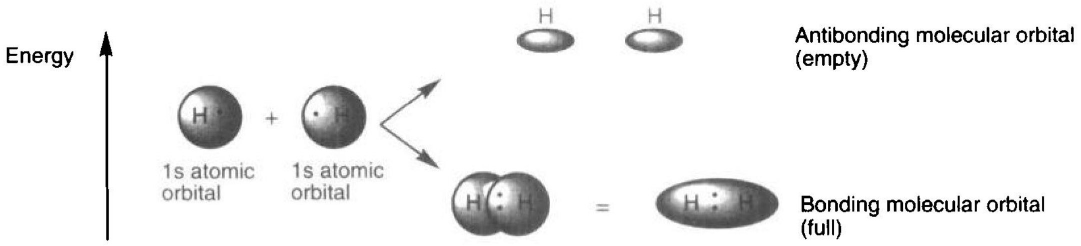
Energy
H
H
Antibonding molecular orbital (empty)
H
H
1s atomic orbital
1s atomic orbital
H : H
=
H : H
Bonding molecular orbital (full)

Fig. 1. Molecular orbitals for hydrogen (H_2).

The MOs are of different energies. One is more stable than the original atomic orbitals and is called the **bonding** MO. The other is less stable and is called the **antibonding** MO. The bonding MO is shaped like a rugby ball and results from the combination of the 1s atomic orbitals. Since this is the more stable MO, the valence electrons (one from each hydrogen) enter this orbital and pair up. The antibonding MO is of higher energy and consists of two deformed spheres. This remains empty. Since the electrons end up in a bonding MO which is more stable than the original atomic orbitals, energy is released and bond formation is favoured. In the subsequent discussions, we shall concentrate solely on the bonding MOs to describe bonding and molecular shape, but it is important to realize that antibonding molecular orbitals also exist.

Sigma bonds

The bonding molecular orbital of hydrogen is an example of a sigma (σ) bond: σ bonds have a circular cross-section and are formed by the head-on overlap of two atomic orbitals. This is a strong interaction and so sigma bonds are strong bonds. In future discussions, we shall see other examples of σ bonds formed by the interaction of atomic orbitals other than the 1s orbital.

Hybridization

Atoms can form bonds with each other by sharing unpaired electrons such that each bond contains two electrons. In Topic A1, we identified that a carbon atom has two unpaired electrons and so we would expect carbon to form two bonds. However, carbon forms four bonds! How does a carbon atom form four bonds with only two unpaired electrons?

So far, we have described the electronic configuration of an isolated carbon atom. However, when a carbon atom forms bonds and is part of a molecular structure, it can 'mix' the *s* and *p* orbitals of its second shell (the valence shell). This is known as **hybridization** and it allows carbon to form the four bonds which we observe in reality.

There are three ways in which this mixing process can take place.

- the 2*s* orbital is mixed with all three 2*p* orbitals. This is known as sp^3 hybridization;
- the 2*s* orbital is mixed with two of the 2*p* orbitals. This is known as sp^2 hybridization;
- the 2*s* orbital is mixed with one of the 2*p* orbitals. This is known as *sp* hybridization.

Section A – Structure and bonding

A3 SP^3 HYBRIDIZATION

Key Notes

Definition	In sp^3 hybridization, the s and the p orbitals of the second shell are 'mixed' to form four hybridized sp^3 orbitals of equal energy.
Electronic configuration	Each hybridized orbital contains a single unpaired electron and so four bonds are possible.
Geometry	Each sp^3 orbital is shaped like a deformed dumbbell with one lobe much larger than the other. The hybridized orbitals arrange themselves as far apart from each other as possible such that the major lobes point to the corners of a tetrahedron. sp^3 Hybridization explains the tetrahedral carbon in saturated hydrocarbon structures.
Sigma bonds	Sigma (σ) bonds are strong bonds formed between two sp^3 hybridized carbons or between an sp^3 hybridized carbon and a hydrogen atom. A σ bond formed between two sp^3 hybridized carbon atoms involves the overlap of half filled sp^3 hybridized orbitals from each carbon atom. A σ bond formed between an sp^3 hybridized carbon and a hydrogen atom involves a half-filled sp^3 orbital from carbon and a half-filled 1s orbital from hydrogen.
Nitrogen, oxygen and chlorine	Nitrogen, oxygen, and chlorine atoms are also sp^3 hybridized in organic molecules. This means that nitrogen has three half-filled sp^3 orbitals and can form three bonds which are pyramidal in shape. Oxygen has two half-filled sp^3 orbitals and can form two bonds which are angled with respect to each other. Chlorine has a single half-filled sp^3 orbital and can only form a single bond. All the bonds which are formed are σ bonds.
Related topics	Covalent bonding and hybridization (A2) Bonds and hybridized centers (A6)

Definition

In sp^3 hybridization, the 2s orbital is mixed with all three of the 2p orbitals to give a set of four sp^3 hybrid orbitals. (The number of hybrid orbitals must equal the number of original atomic orbitals used for mixing.) The hybrid orbitals will each have the same energy but will be different in energy from the original atomic orbitals. That energy difference will reflect the mixing of the respective atomic orbitals. The energy of each hybrid orbital is greater than the original s orbital but less than the original p orbitals (*Fig. 1*).

Electronic configuration

The valence electrons for carbon can now be fitted into the sp^3 hybridized orbitals (*Fig. 1*). There was a total of four electrons in the original 2s and 2p orbitals. The s orbital was filled and two of the p orbitals were half filled. After hybridization, there is a total of four hybridized sp^3 orbitals all of equal energy. By Hund's rule, they are all half filled with electrons which means that there are four unpaired electrons. Four bonds are now possible.

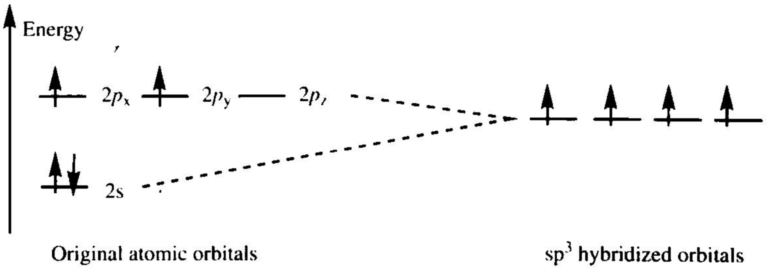
Energy
$2p_x$
$2p_y$
$2p_z$
2s
Original atomic orbitals
sp^3 hybridized orbitals

Fig. 1. sp^3 *Hybridization.*

Geometry

Each of the sp^3 hybridized orbitals has the same shape – a rather deformed looking dumbbell (*Fig. 2*). This deformed dumbbell looks more like a *p* orbital than an *s* orbital since more *p* orbitals were involved in the mixing process.

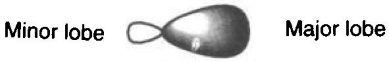
Minor lobe
Major lobe

Fig. 2. sp^3 *Hybridized orbital.*

Each sp^3 orbital will occupy a space as far apart from each other as possible by pointing to the corners of a tetrahedron (*Fig. 3*). Here, only the major lobe of each hybridized orbital has been shown and the angle between each of these lobes is 109.5°. This is what is meant by the expression **tetrahedral carbon**. The three-dimensional shape of the tetrahedral carbon can be represented by drawing a normal line for bonds in the plane of the page. Bonds going behind the page are represented by a hatched wedge, and bonds coming out the page are represented by a solid wedge.

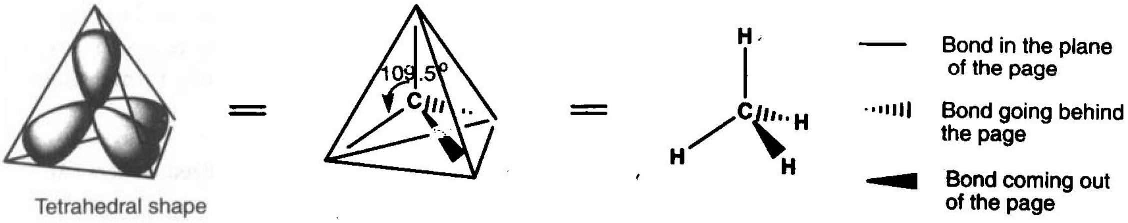
Tetrahedral shape
=
109.5°
C
=
H
C
H
H
H
Bond in the plane of the page
Bond going behind the page
Bond coming out of the page

Fig. 3. Tetrahedral shape of an sp^3 *hybridized carbon*

Sigma bonds

A half-filled sp^3 hybridized orbital from one carbon atom can be used to form a bond with a half-filled sp^3 hybridized orbital from another carbon atom. In *Fig. 4a*, the major lobes of the two sp^3 orbitals overlap directly leading to a strong σ bond. It is the ability of hybridized orbitals to form strong σ bonds that explains why hybridization takes place in the first place. The deformed dumbbell shapes allow a much better orbital overlap than would be obtained from a pure *s* orbital or a pure *p* orbital. A σ bond between an sp^3 hybridized carbon atom and a hydrogen atom involves the carbon atom using one of its half-filled sp^3 orbitals and the hydrogen atom using its half-filled 1*s* orbital (*Fig. 4b*).

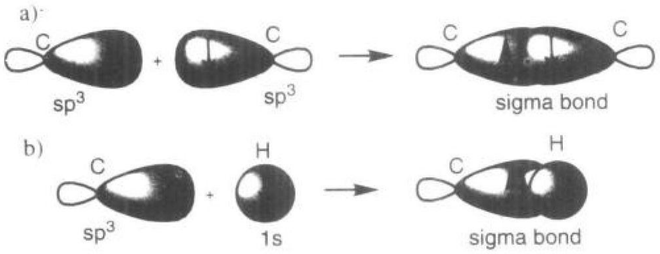

Fig. 4. (a) σ Bond between two sp^3 *hybridized carbons; (b) σ bond between an* sp^3 *hybridized carbon and hydrogen*

Nitrogen, oxygen, and chlorine

Nitrogen, oxygen and chlorine atoms can also be sp^3 hybridized in organic structures. Nitrogen has five valence electrons in its second shell. After hybridization, it will have three half-filled sp^3 orbitals and can form three bonds. Oxygen has six valence electrons. After hybridization, it will have two half-filled sp^3 orbitals and will form two bonds. Chlorine has seven valence electrons. After hybridization, it will have one half-filled sp^3 orbital and will form one bond.

The four sp^3 orbitals for these three atoms form a tetrahedral arrangement with one or more of the orbitals occupied by a lone pair of electrons. Considering the atoms alone, nitrogen forms a pyramidal shape where the bond angles are slightly less than 109.5° (c. 107°) (*Fig. 5a*). This compression of the bond angles is due to the orbital containing the lone pair of electrons, which demands a slightly greater amount of space than a bond. Oxygen forms an angled or bent shape where two lone pairs of electrons compress the bond angle from 109.5° to c. 104° (*Fig. 5b*).

Alcohols, amines, alkyl halides, and ethers all contain sigma bonds involving nitrogen, oxygen, or chlorine. Bonds between these atoms and carbon are formed by the overlap of half-filled sp^3 hybridized orbitals from each atom. Bonds involving hydrogen atoms (e.g. O–H and N–H) are formed by the overlap of the half-filled 1*s* orbital from hydrogen and a half-filled sp^3 orbital from oxygen or nitrogen.

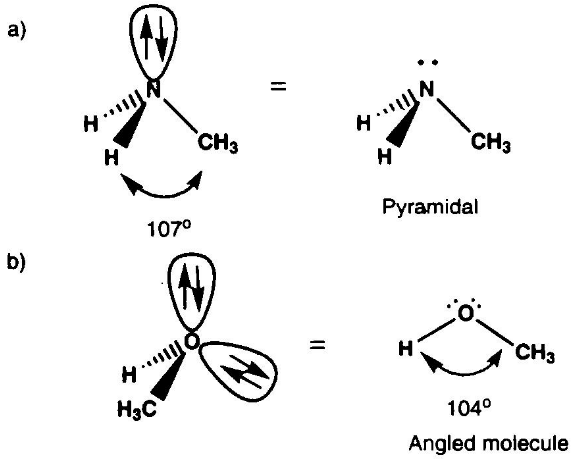

Fig. 5. (a) Geometry of sp^3 *hybridized nitrogen; (b) geometry of* sp^3 *hybridized oxygen.*

A4 SP^2 HYBRIDIZATION

Key Notes

Definition	In sp^2 hybridization, a $2s$ orbital is 'mixed' with two of the $2p$ orbitals to form three hybridized sp^2 orbitals of equal energy. A single $2p$ orbital is left over which has a slightly higher energy than the hybridized orbitals.
Electronic configuration	For carbon, each sp^2 hybridized orbital contains a single unpaired electron. There is also a half-filled $2p$ orbital. Therefore, four bonds are possible.
Geometry	Each sp^2 orbital is shaped like a deformed dumbbell with one lobe much larger than the other. The remaining $2p$ orbital is a symmetrical dumbbell. The major lobes of the three sp^2 hybridized orbitals point to the corners of a triangle, with the $2p$ orbital perpendicular to the plane.
Alkenes	Each sp^2 hybridized carbon forms three σ bonds using three sp^2 hybridized orbitals. The remaining $2p$ orbital overlaps 'side on' with a neighboring $2p$ orbital to form a pi (π) bond. The π bond is weaker than the σ bond, but is strong enough to prevent rotation of the C=C bond. Therefore, alkenes are planar, with each carbon being trigonal planar.
Carbonyl groups	The oxygen and carbon atoms are both sp^2 hybridized. The carbon has three sp^2 hybridized orbitals and can form three σ bonds, one of which is to the oxygen. The oxygen has one sp^2 orbital which is used in the σ bond with carbon. The p orbitals on carbon and oxygen are used to form a π bond.
Aromatic rings	Aromatic rings are made up of six sp^2 hybridized carbons. Each carbon forms three σ bonds which results in a planar ring. The remaining $2p$ orbital on each carbon is perpendicular to the plane and can overlap with a neighboring $2p$ orbital on either side. This means that a molecular orbital is formed round the whole ring such that the six π electrons are delocalized around the ring. This results in increased stability such that aromatic rings are less reactive than alkenes.
Conjugated systems	Conjugated systems such as conjugated alkenes and α,β-unsaturated carbonyl compounds involve alternating single and double bonds. In such systems, the p orbitals of one π bond are able to overlap with the p orbitals of a neighboring π bond, and thus give a small level of double bond character to the connecting bond. This partial delocalization gives increased stability to the conjugated system.

Related topics

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