Information

Discipline: Bioorganic chemistry

Final assessment: test

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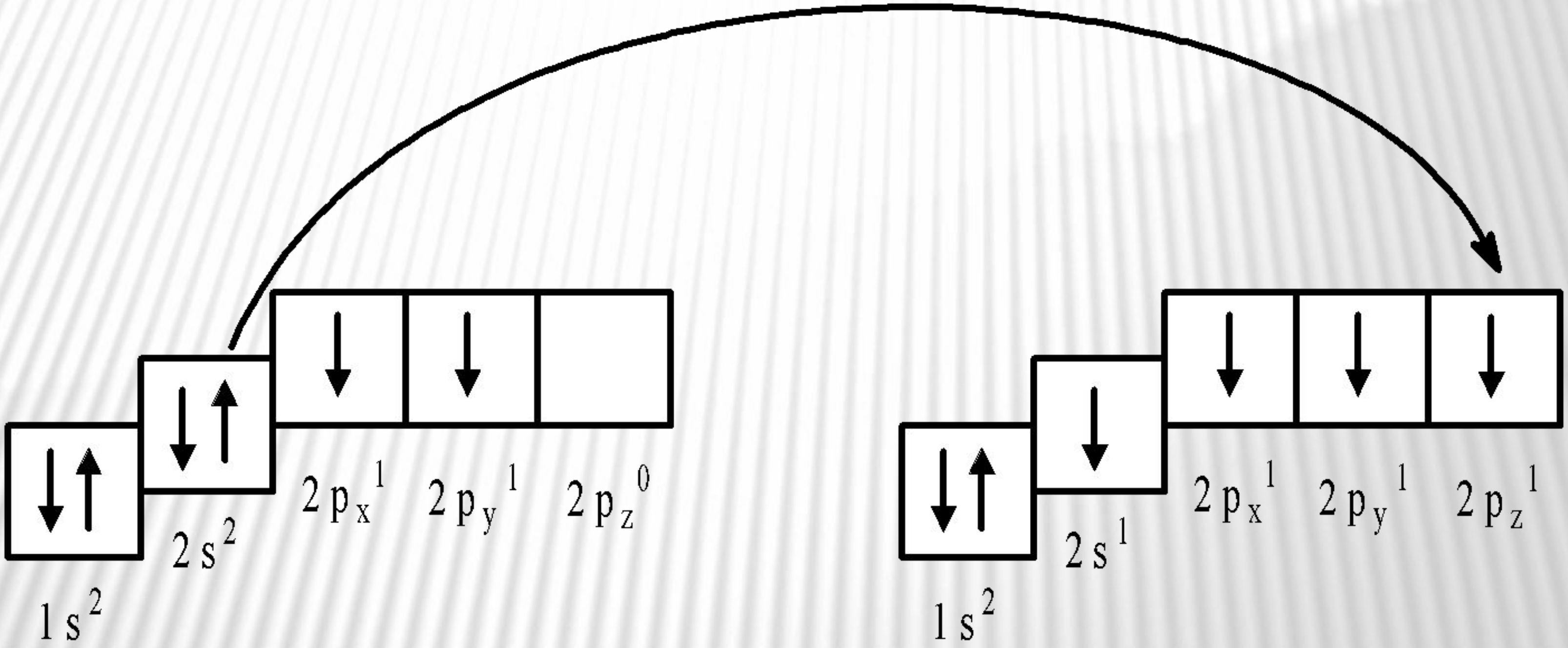
General aspects of chemical structure and reactivity of organic compounds

Lecture №1

Chemical bonding and mutual atoms' influence in organic molecules

Electronic configuration of carbon atom in organic molecules

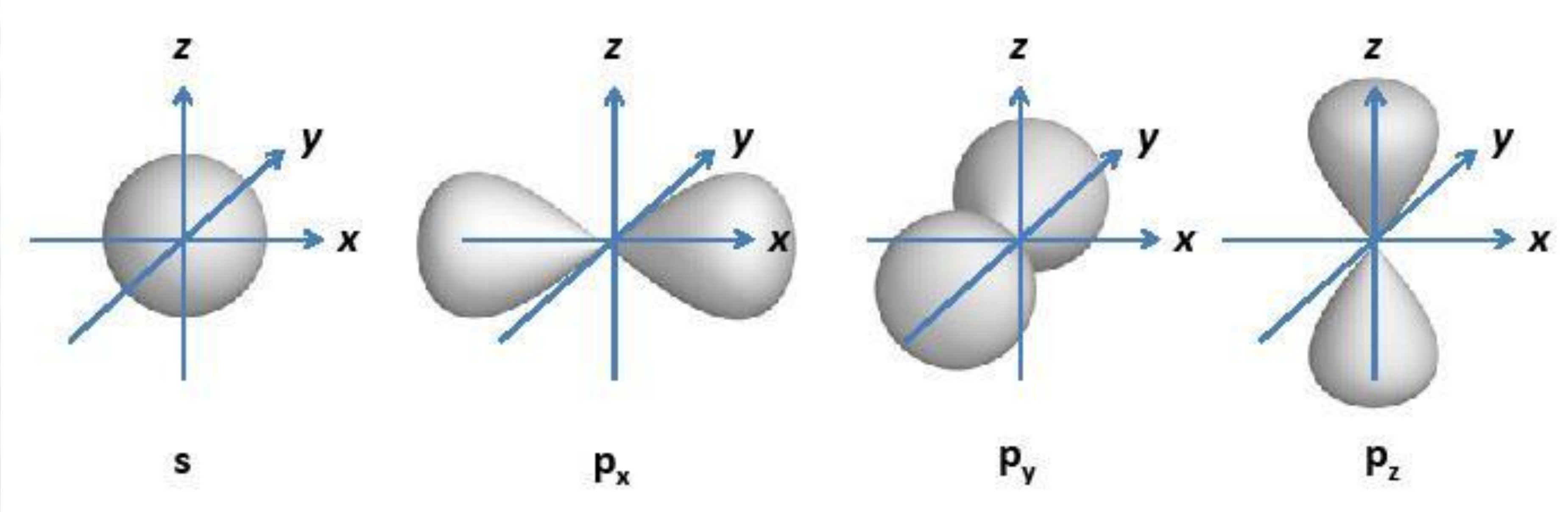


ground state

excited state

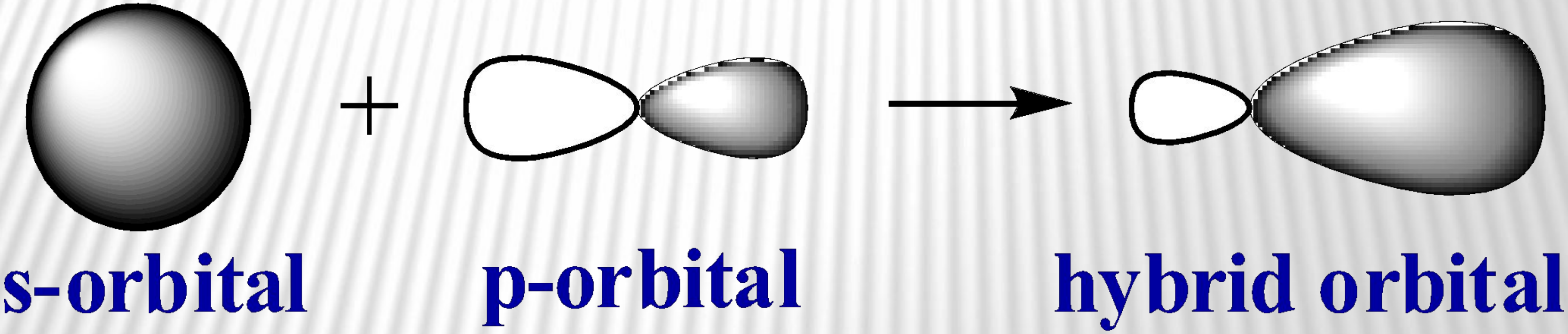
Atomic orbitals

The orbital is a region of space where the probability of finding an electron is large, above 95% of its time.

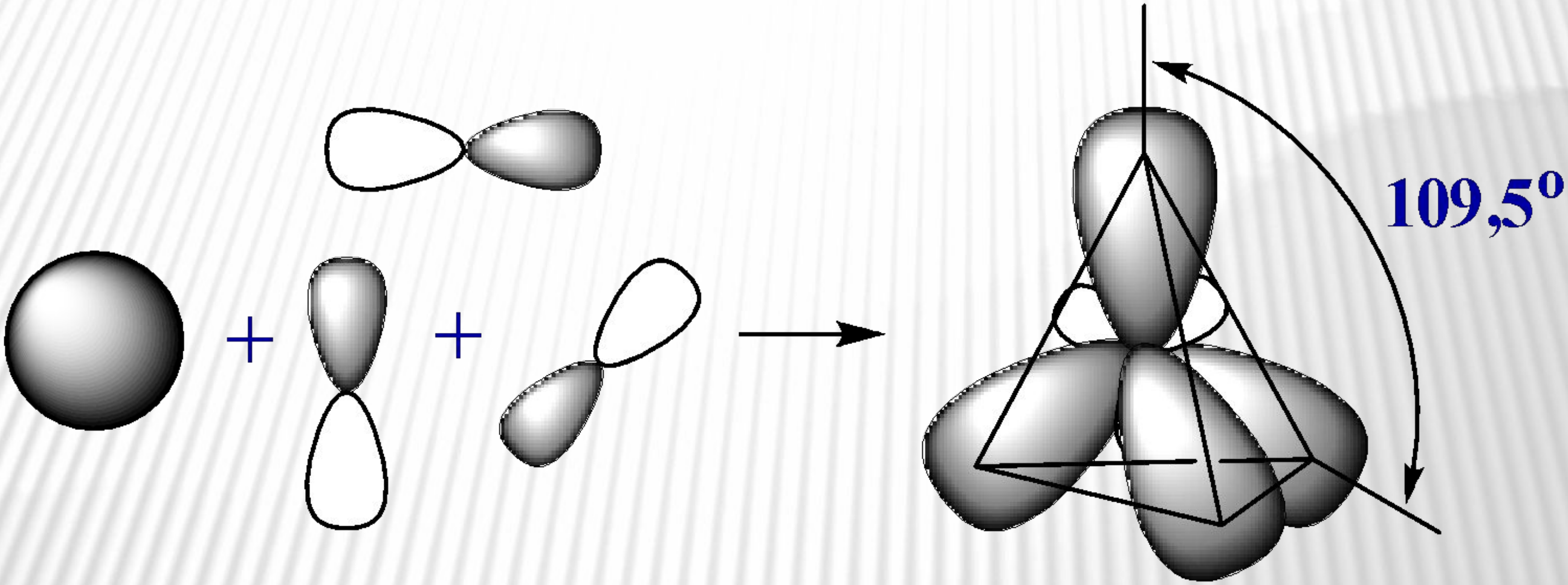


Hybridization of orbitals

Hybridization **is the process of atomic orbitals alignment in form and energy.**



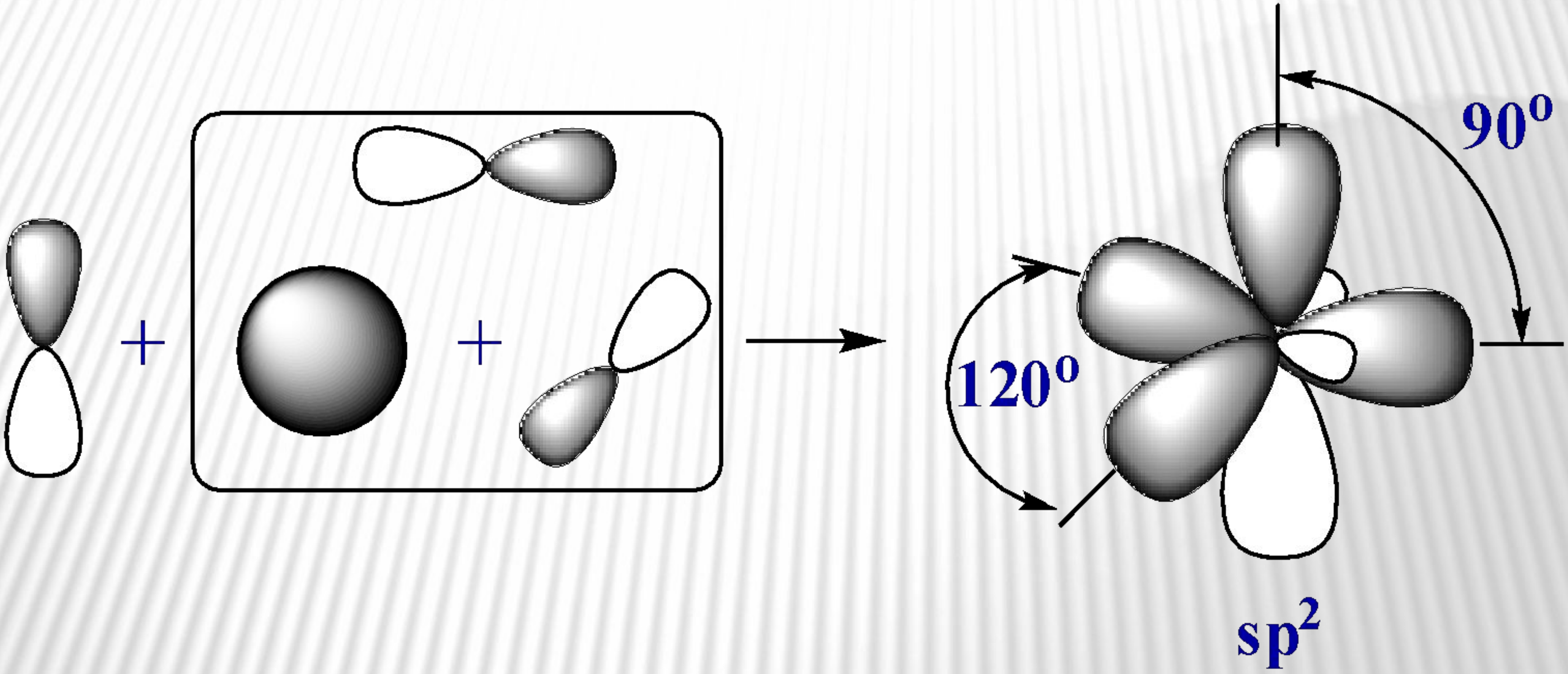
sp^3-Hybridization



sp^3

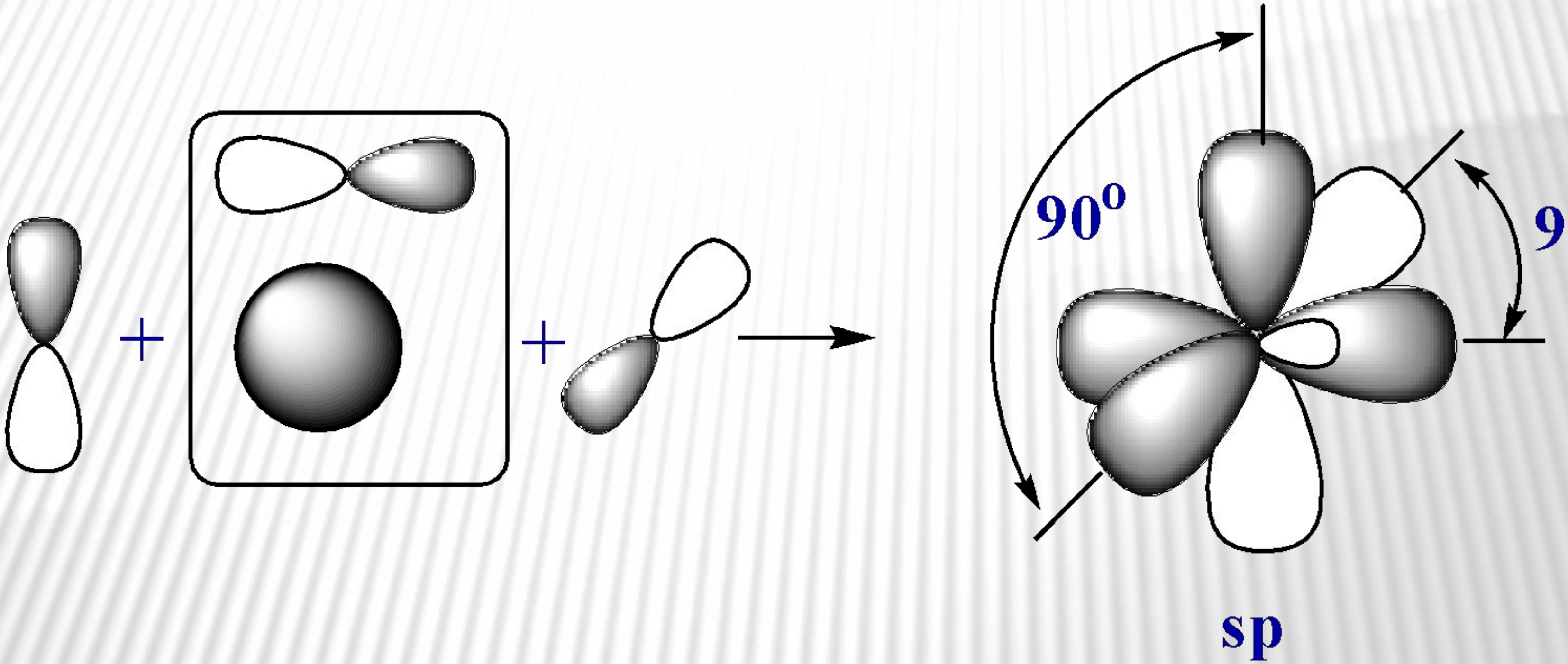
tetrahedral configuration

sp^2-Hybridization



planar configuration

sp-Hybridization



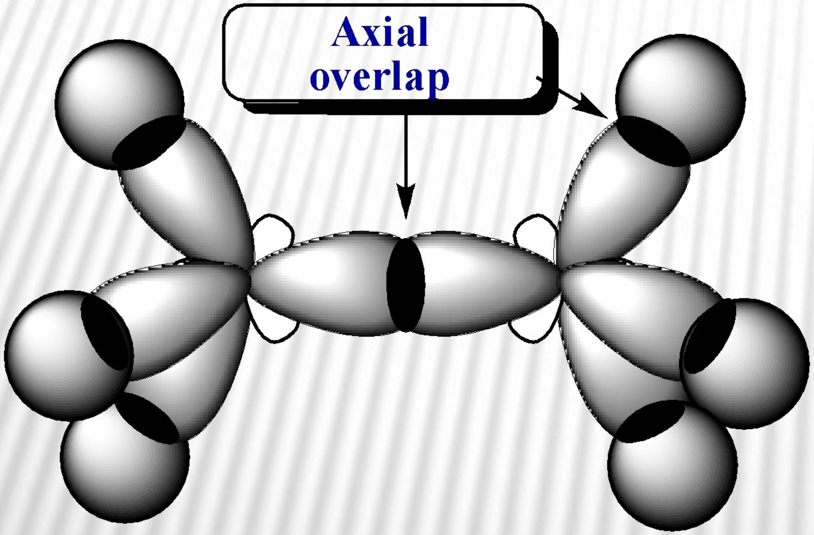
linear configuration

Chemical bonds in organic compounds

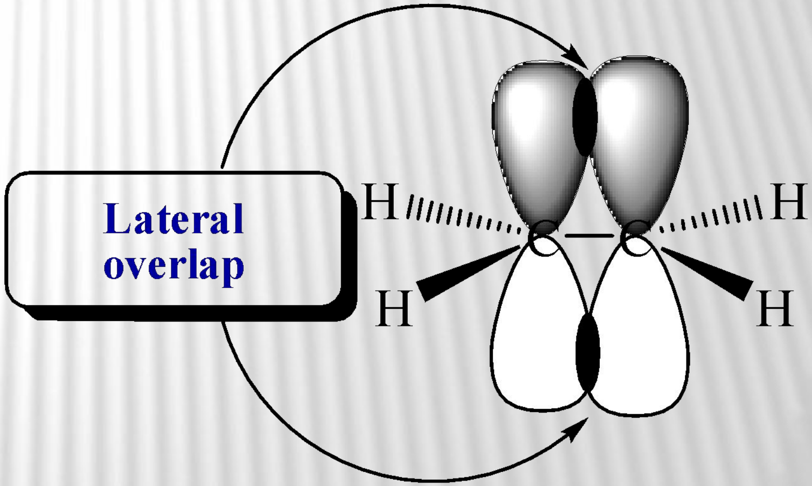
Covalent bonds

σ - bond

π - bond



Axial overlap



Lateral overlap

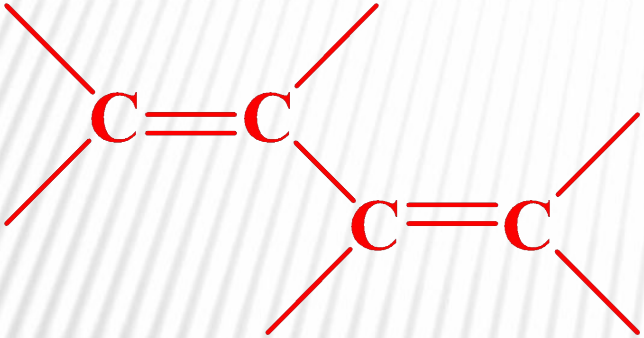
Conjugation

Conjugation is the formation of delocalized electronic cloud in molecule as a result of *p*-orbitals overlap.

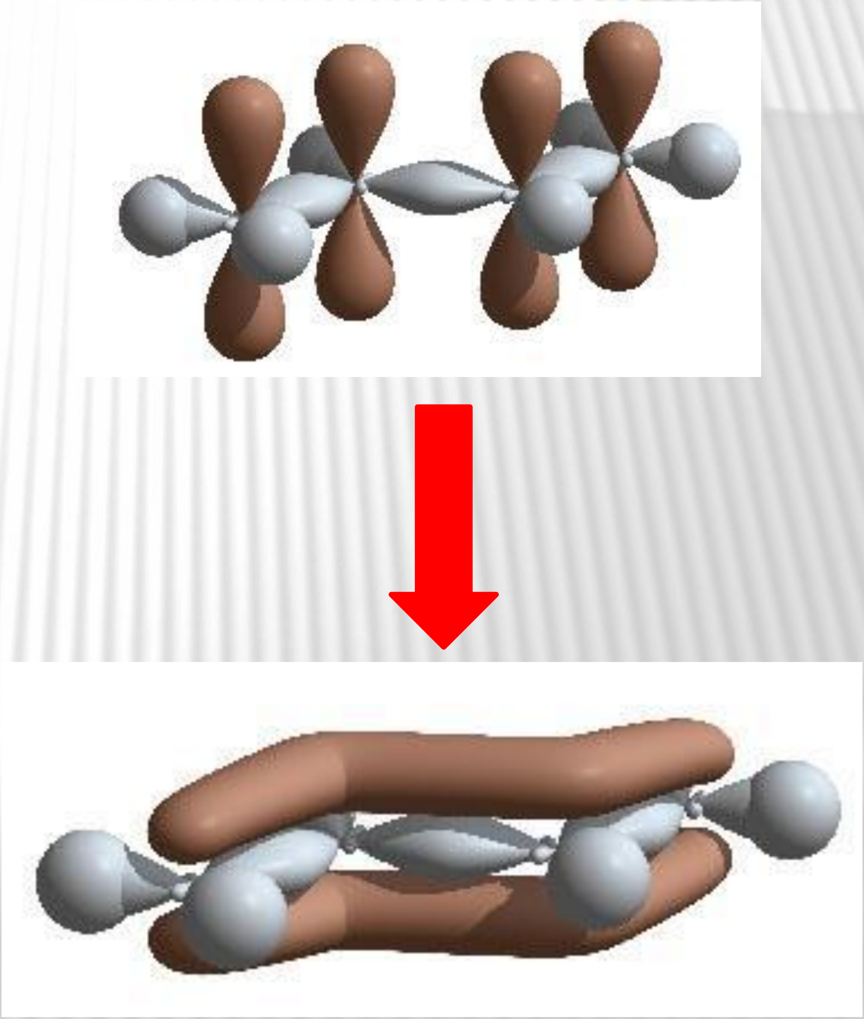
π,π-Conjugation is the type of orbital interaction when the *p*-orbitals are delocalized over the entire *π* system.

p,π-Conjugation is the overlap of a p-orbital on an atom adjacent to a double bond.

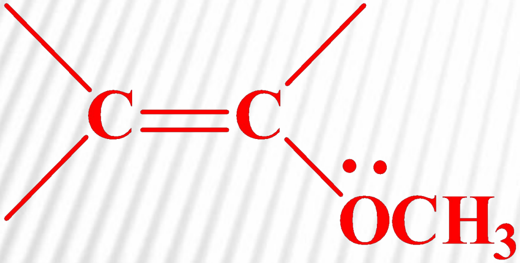
π,π-Conjugation



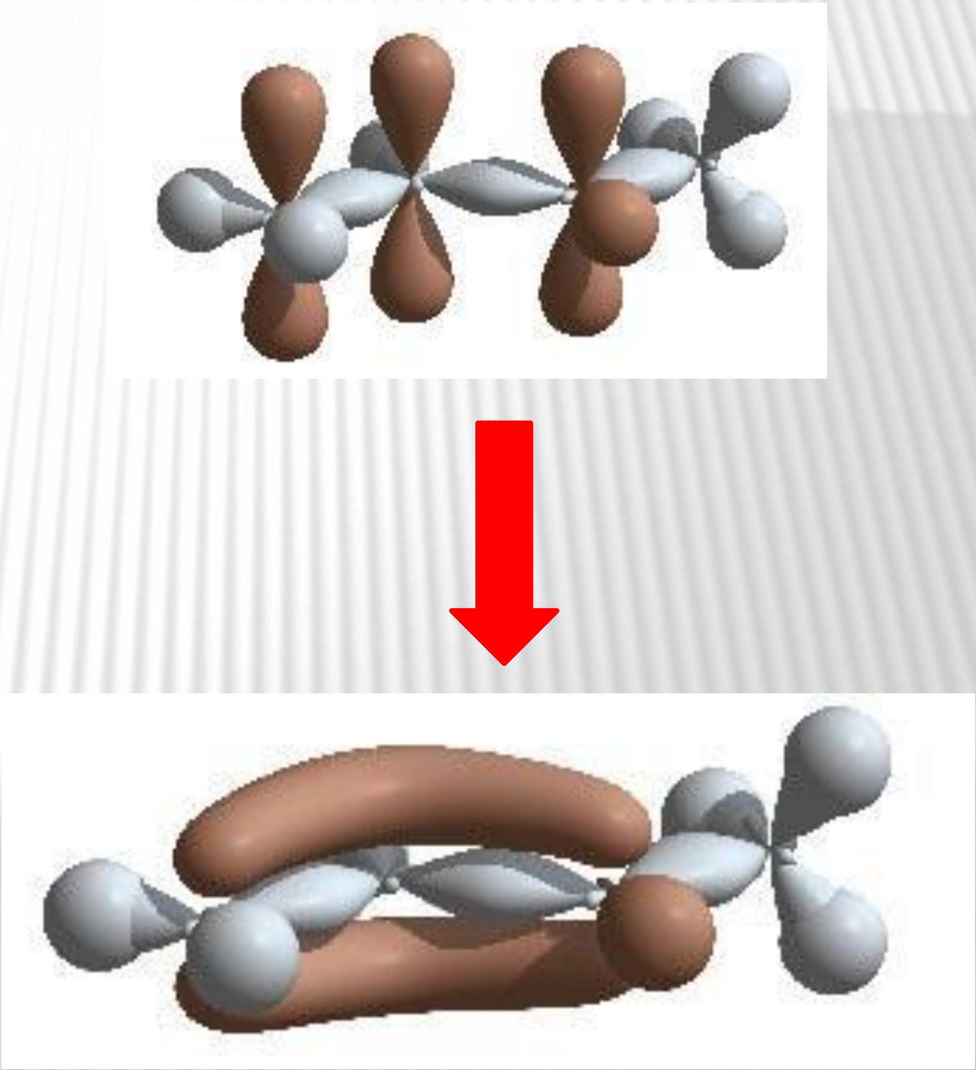
butadiene-1,3



p,π-Conjugation

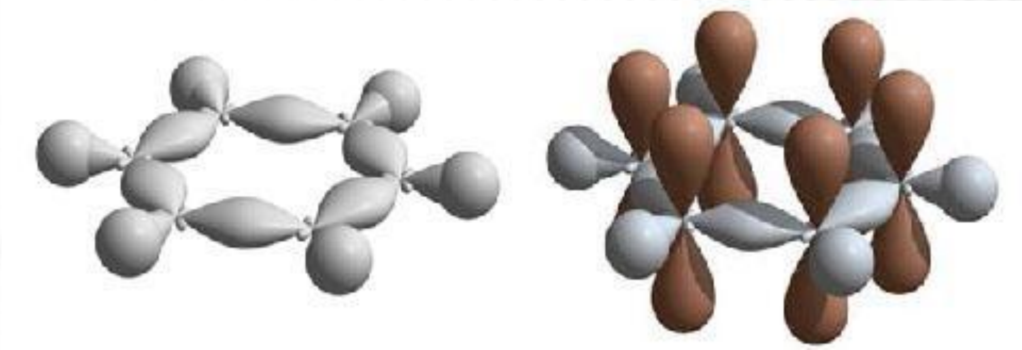


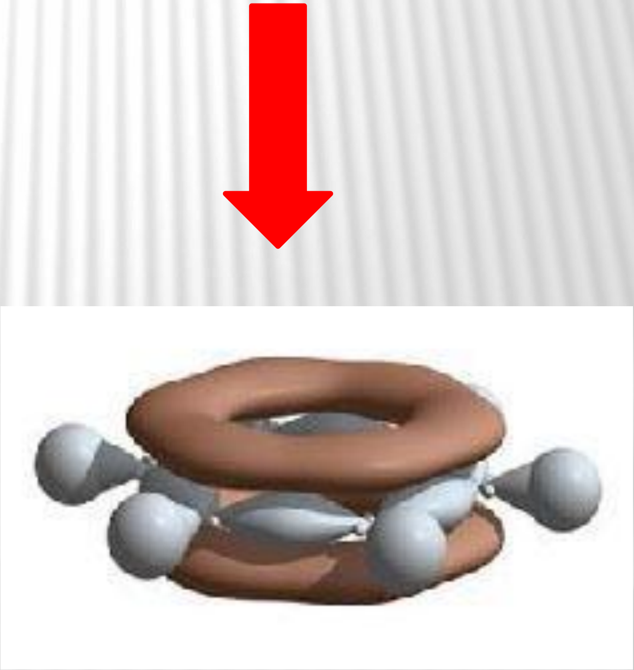
methyl vinyl ether



Aromaticity

benzene





A molecule can be aromatic only if it has a planar cyclic system of conjugation with a p-orbital on each atom and only if the *p*-orbital system contains $(4n+2)$ π-electrons, where *n* is an integer (0, 1, 2, 3, etc.).

Inductive effect

Inductive effect (I) **is the shifting of electrons in a σ-bond in response to electronegativity of nearby atoms.**

- **present in any polar molecule;**
- **decrease and fade after 2-3 bonds.**

$CH_3\rightarrow CH_2\rightarrow Cl$ $CH_3\leftarrow CH_2\leftarrow MgCl$

-I-effect **+I-effect**

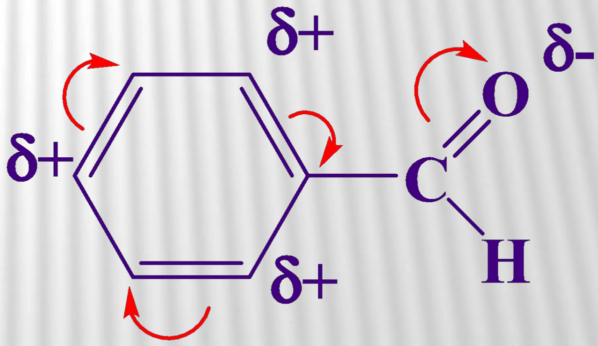
Mesomeric effect

Mesomeric effect (M) is the shifting of electron density caused by a substituent in conjugation system through p-orbital overlap.

- present only in conjugation systems;
- distribute throughout the conjugated system.

$CH_2=CH-\ddot{N}H_2$

+M-effect



-M-effect

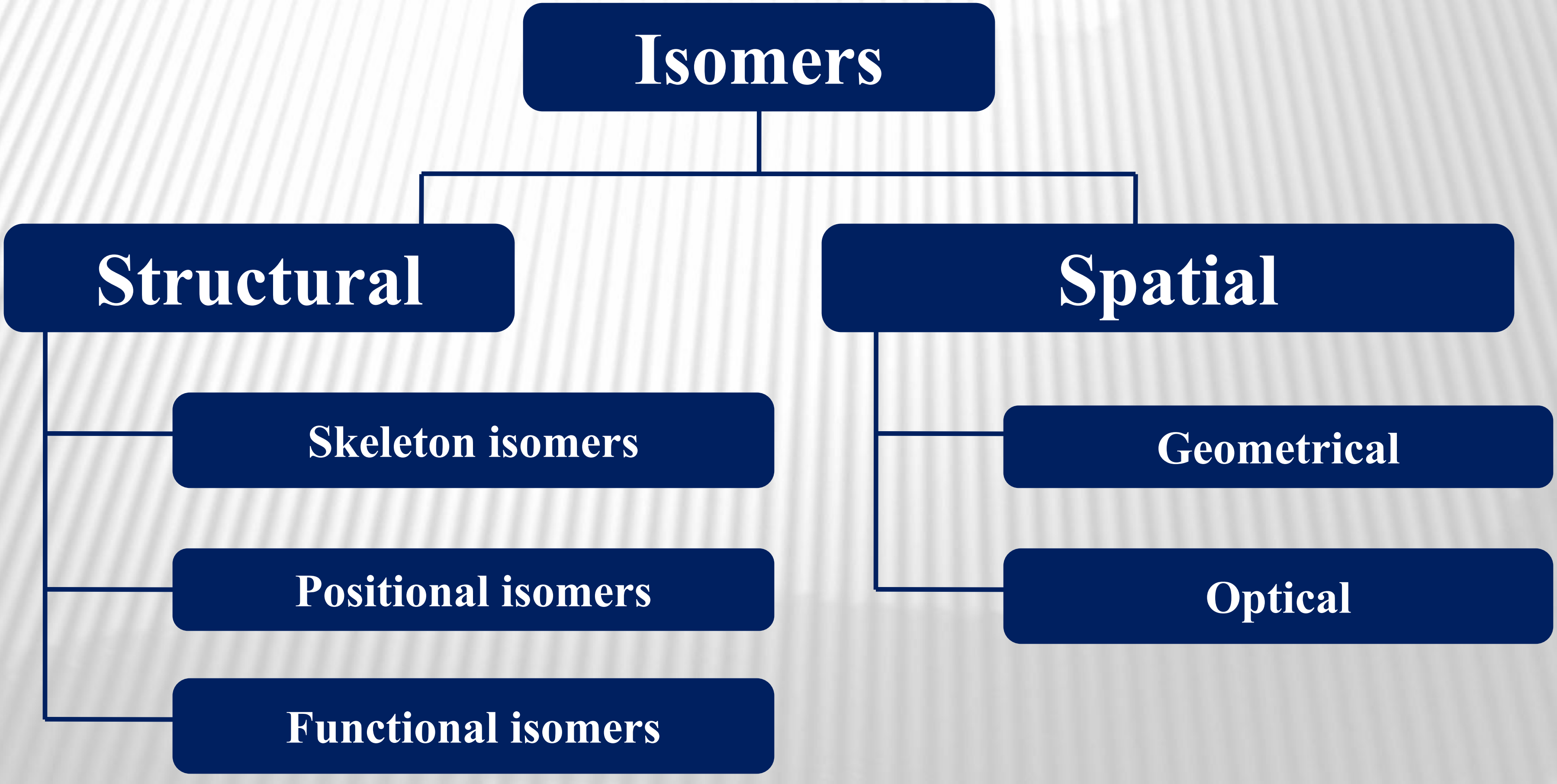
Electron donors (D) and electron withdrawers (W)

Substituent	Electronic effects		Type of substituent
	inductive	mesomeric	
Alkyl- (R)	*+I*	-	**D**
$-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OR$	*-I*	*+M*	$+M > -I$ **D**
Halogens	*-I*	*+M*	$-I > +M$ **W**
$-NO_2$, $-COOH$, $-CN$, $-SO_3H$, $>C=O$	*-I*	*-M*	**W**

Spatial structure of organic compounds

Isomerism of organic compounds

Isomers are the compounds which have the same composition but different sequence of atoms or their location in space, therefore have different properties.



Isomers

Structural

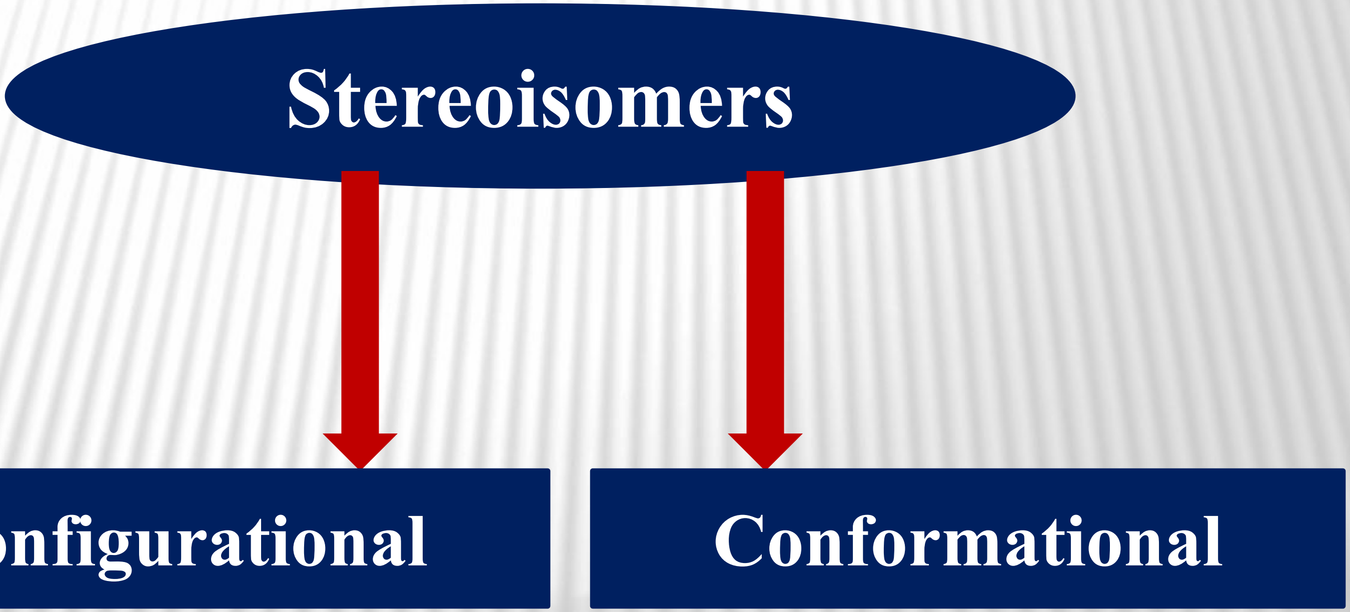
- Skeleton isomers
- Positional isomers
- Functional isomers

Spatial

- Geometrical
- Optical

Stereoisomerism

Stereoisomers are the compounds that have the same order of atoms attachment but differ only in the arrangement of their atoms or groups in space.



Stereoisomers

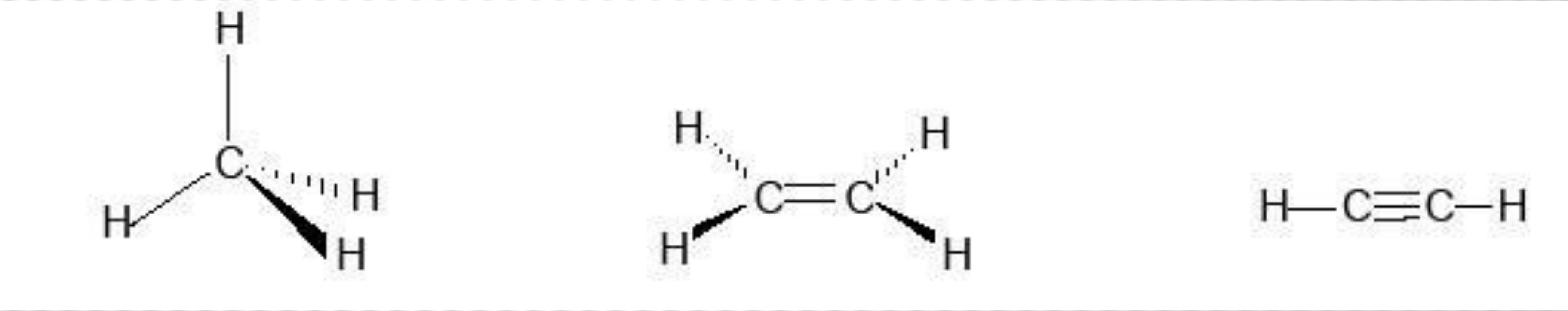
Configurational

Conformational

Configuration of molecules

Configuration **is the arrangement of atoms and groups in space without regard to arrangements that differ only due to rotation about one or more single bonds.**

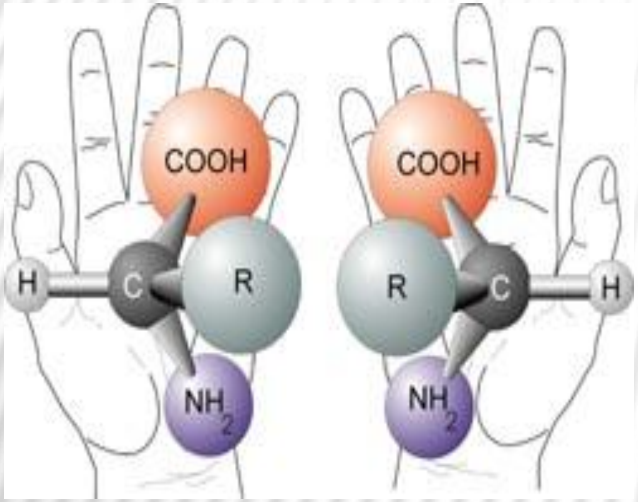
Carbon atom configurations



tetrahedral **planar** **linear**

Chirality

Chirality **is the property of the object to be nonsuperposable with its mirror image.**



The simple example of chirality is presence the chiral center in molecule.

It may be carbon atom with four different atoms or groups - *asymmetric carbon atom (*C).*

Such molecules have optical activity – they rotate the plane of polarized light.

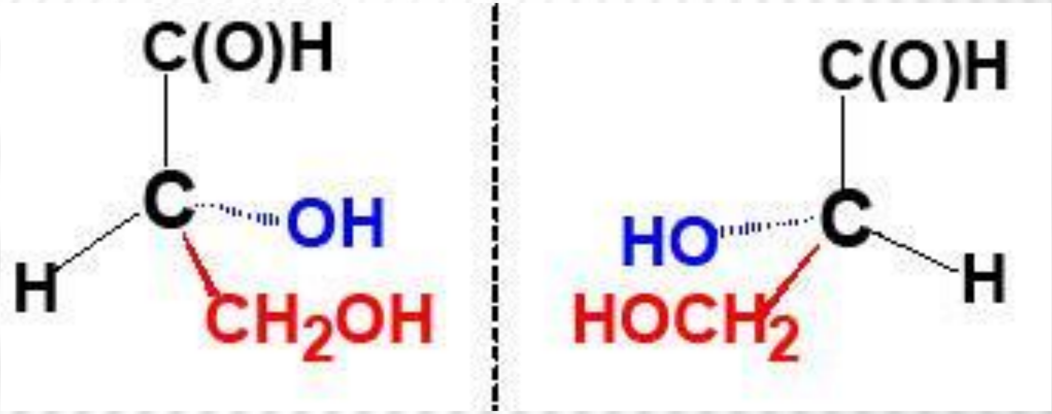
Types of isomers:

- **enantiomers**
- **diastereomers**

Enantiomers

Enantiomers **are the stereoisomers, the molecules of which relate to each other as an object and its nonsuperposable mirror image.**

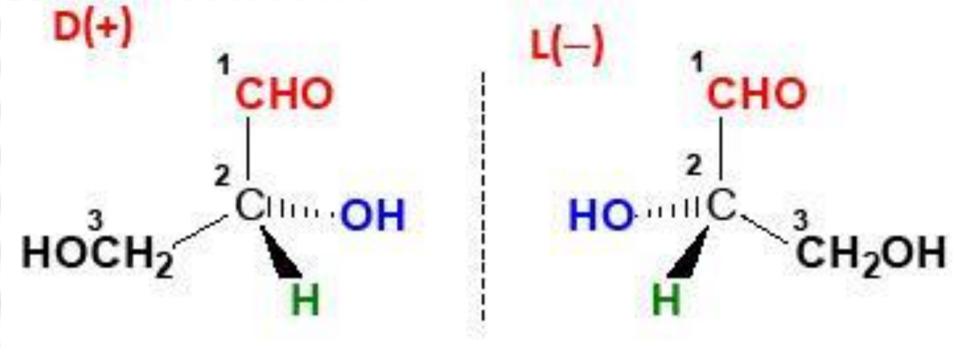
- ✔ **enantiomers have the same physical and chemical properties;**
- ✔ **enantiomers have optical activity.**



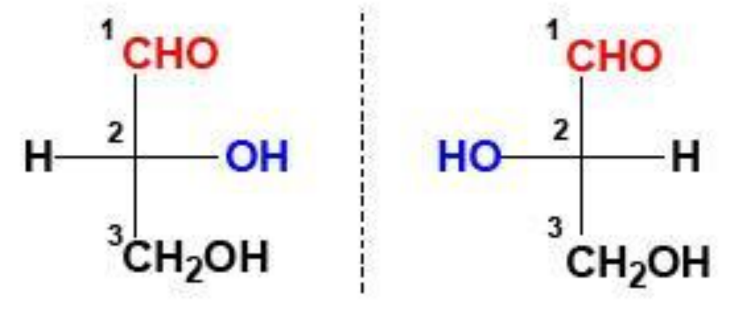
Enantiomers of glyceraldehyde

Racemate **is a mixture containing equal amounts of both enantiomers. Racemic mixture is optically inactive.**

Fischer projections



Spatial formulas



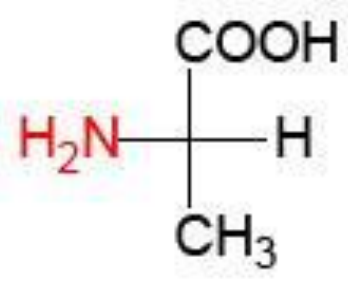
Fischer projections

Rules

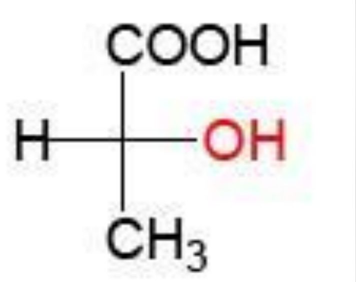
- the carbon chain is disposed vertically (with the principle group at the top);
- substituents on the horizontal line lie in front of the plane, on vertical line– behind the plane of the paper;
- two interchanges do not alter the initial configuration;
- the rotation of projection through 180° in the plane of the paper do not alter the initial configuration.

D,*L*-Nomenclature

- Glyceraldehyde is the configurational standard.
- Fischer projection writes in “standard view”. We can do the interchanges or rotate the projection through 180º to achieve the “standard view”.
- If the group lies on the left side we name it as levorotatory enantiomer (*L*). If the group lies on the right side we name it as dextrorotatory enantiomer (*D*).



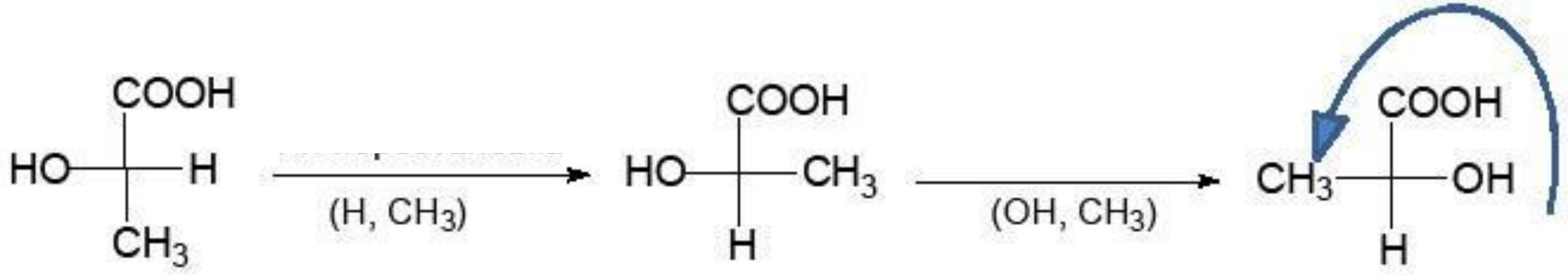
L-alanine



D-lactic acid

R,*S*-Nomenclature

- ✔ The least substituent near the chiral center must lie at the bottom of the Fischer projection.
- ✔ Atoms attached directly to the chiral center are first arranged according to decreased atomic number.
- ✔ If the remaining three groups are arranged clockwise, the configuration is symbolized by ***R***. If they form a counterclockwise array, the configuration is symbolized by ***S***.



***L*-lactic acid**

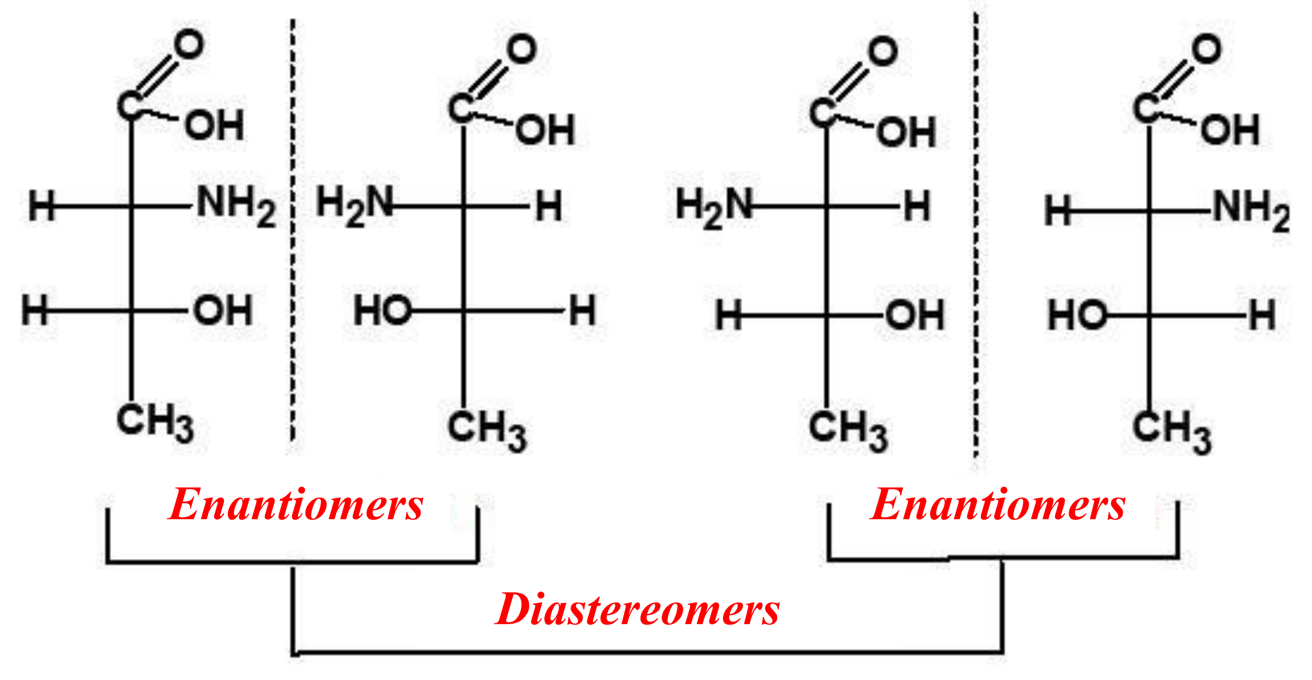
(*S*)-lactic acid

Diastereomers

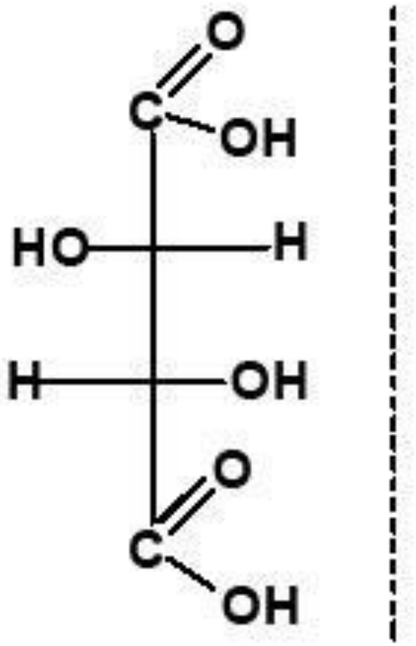
Diastereomers **are the stereoisomers that are not mirror images of one another.**

- ✔ **they have different physical and chemical properties.**

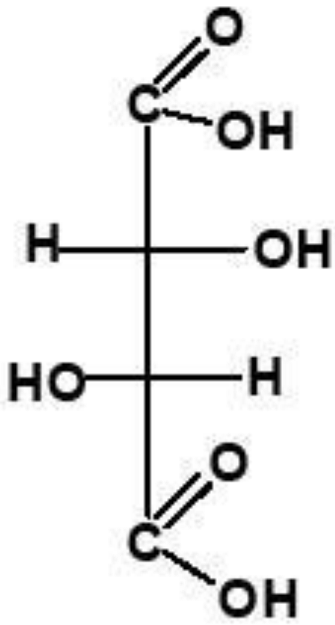
If a molecule has *n* chiral centers, the total number of stereoisomers will be $N = 2^n$.



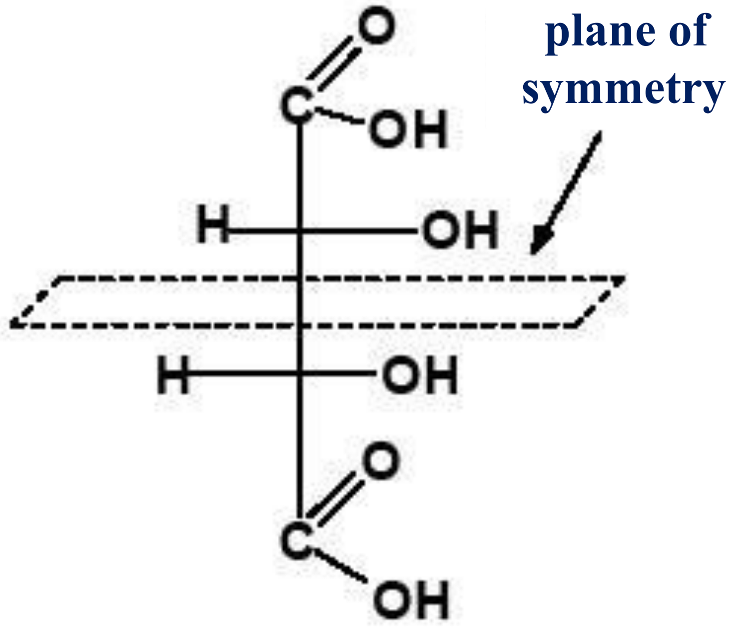
meso Compounds



L-tartaric acid



D-tartaric acid



meso-tartaric acid

A meso compound is an optically inactive achiral stereoisomer containing chiral centers.

Acidity and basicity of organic compounds

Acidity and basicity **are the key notions, determining many fundamental physico-chemical and biochemical properties of organic compounds.**

Brønstedt-Lowry concept

J.-N. Brønstedt

An acid **is a neutral molecule or an ion that can donate a proton.**

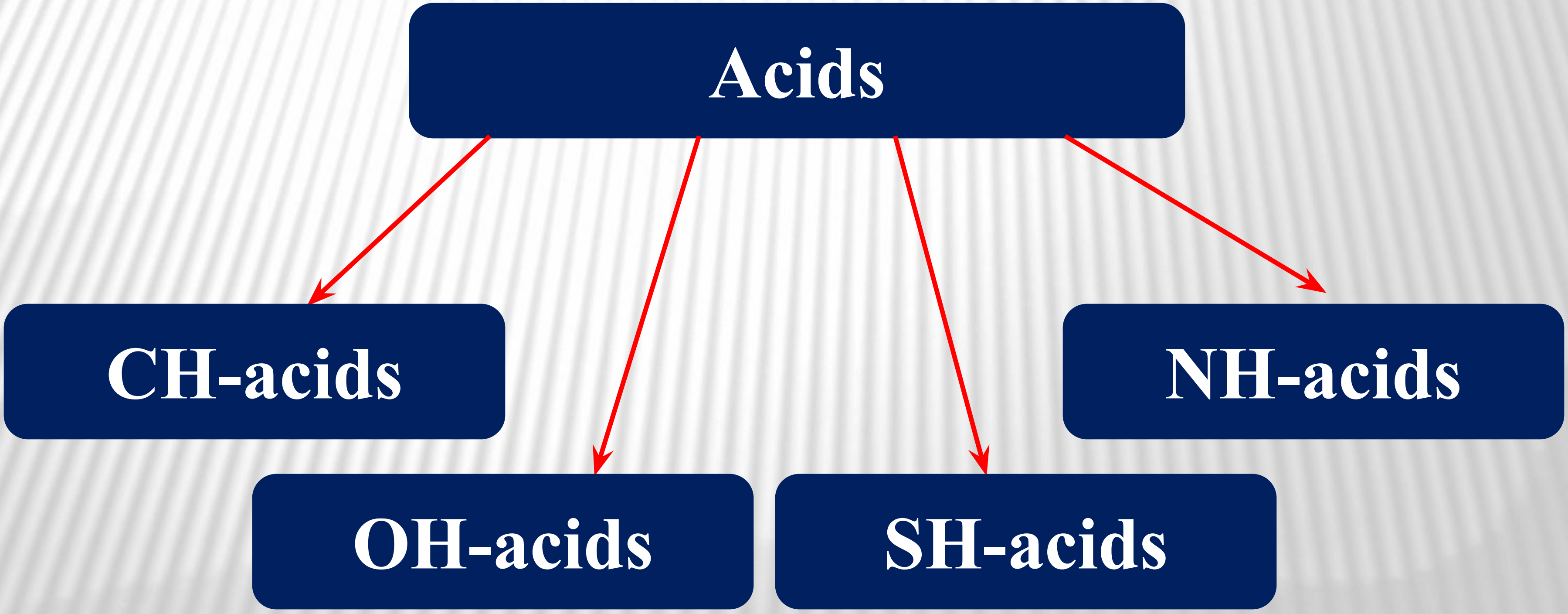
A base **is a neutral molecule or an ion that can accept a proton.**

T. M. Lowry

$$\underset{\text{acid}}{AH} + \underset{\text{base}}{:B} = \underset{\text{conjugate base}}{A^-} + \underset{\text{conjugate acid}}{BH^+}$$

Brønstedt acids

Acidic site **is a part of molecule that involves hydrogen together with an atom attached to it.**



Acids

CH-acids

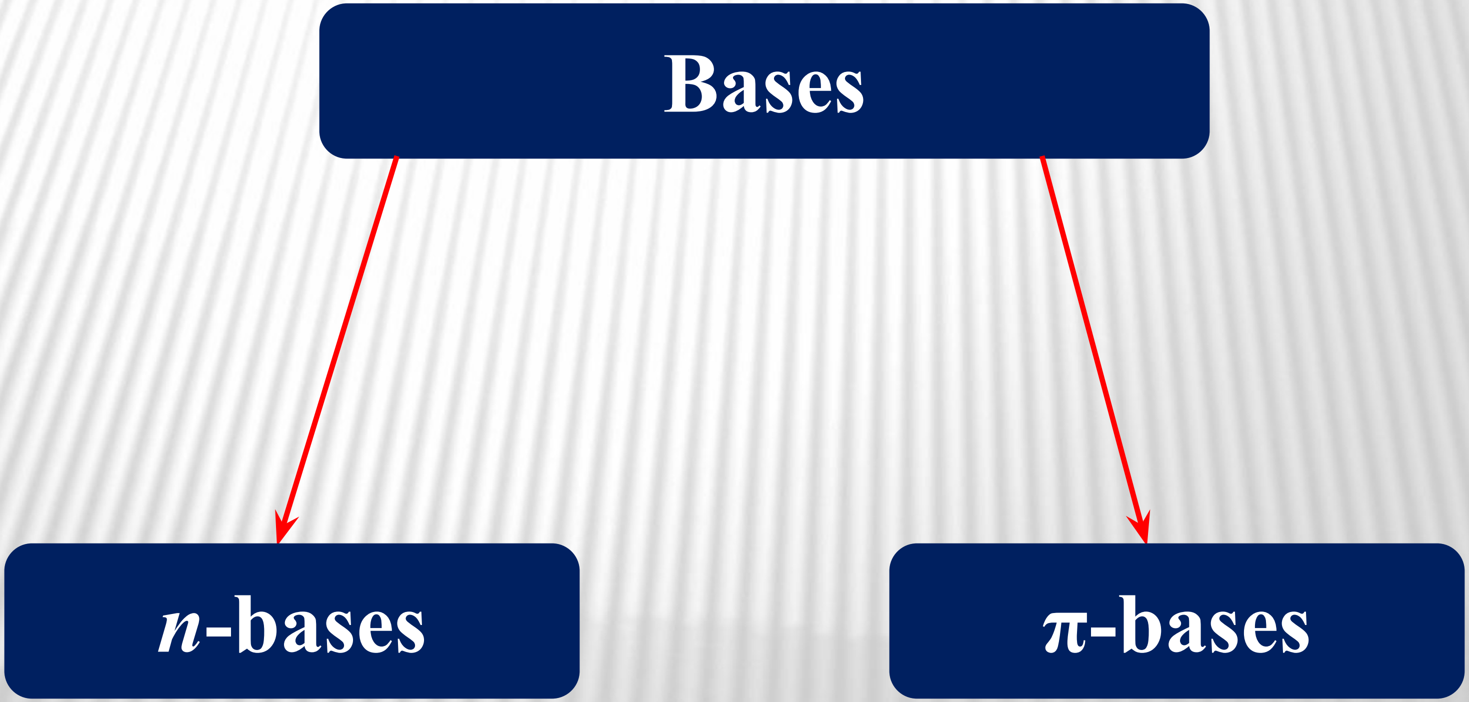
OH-acids

SH-acids

NH-acids

Brønstedt bases

Basic site **is a heteroatom with a lone-pair of electrons or a π-bond which are capable to accept a proton.**



Bases

***n*-bases**

π-bases

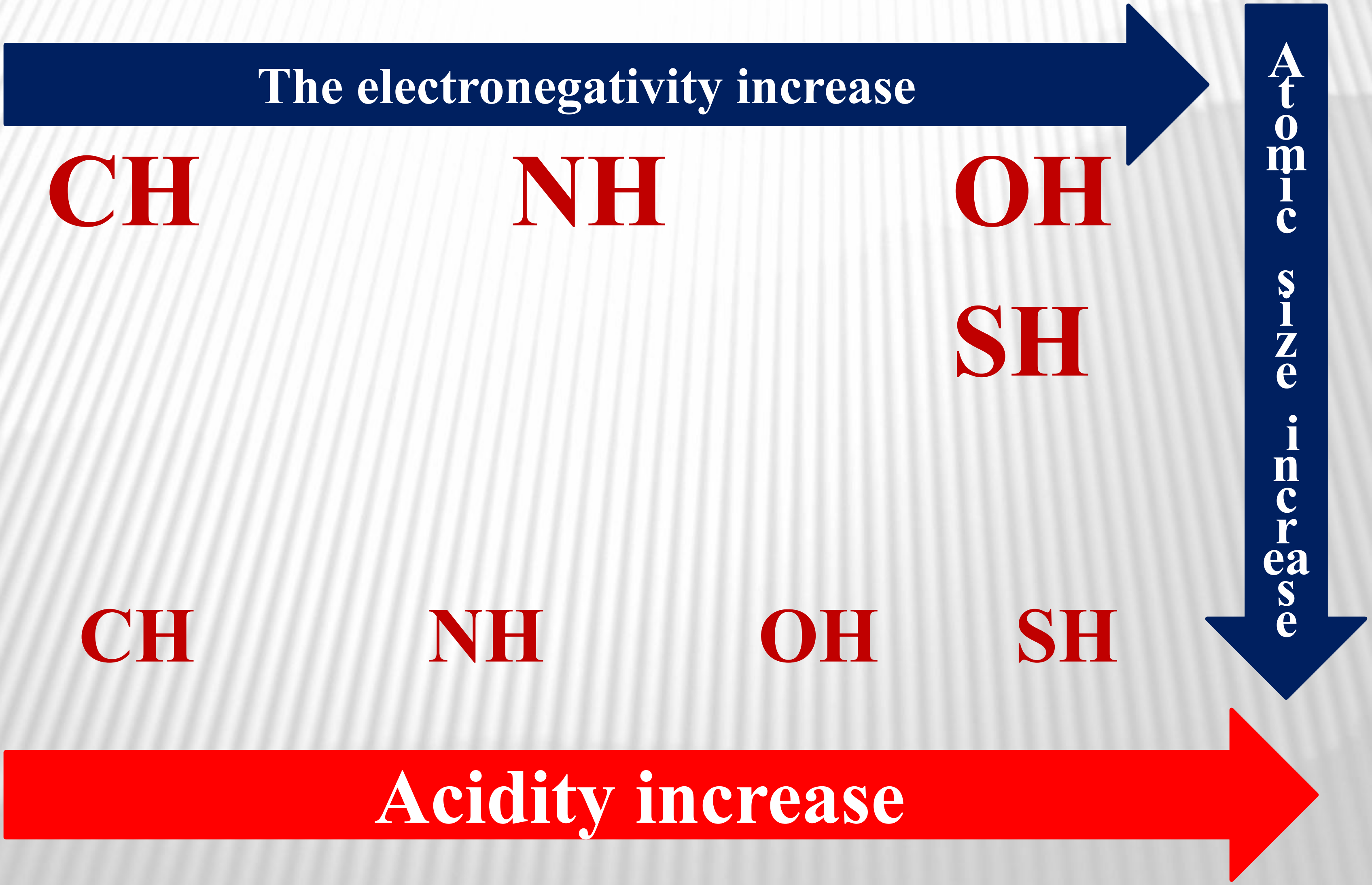
Comparison the acidity

The more stable is an anion, the stronger is an acid!

The factors which influence the stability of conjugate bases:

- ✓ electronegativity and polarizability of the atom in the acidic site;
- ✓ delocalization of a negative charge due to the effect of substituens in a molecule;
- ✓ solvation effects.

The influence of atom nature in acidic site



The electronegativity increase

CH NH OH

SH

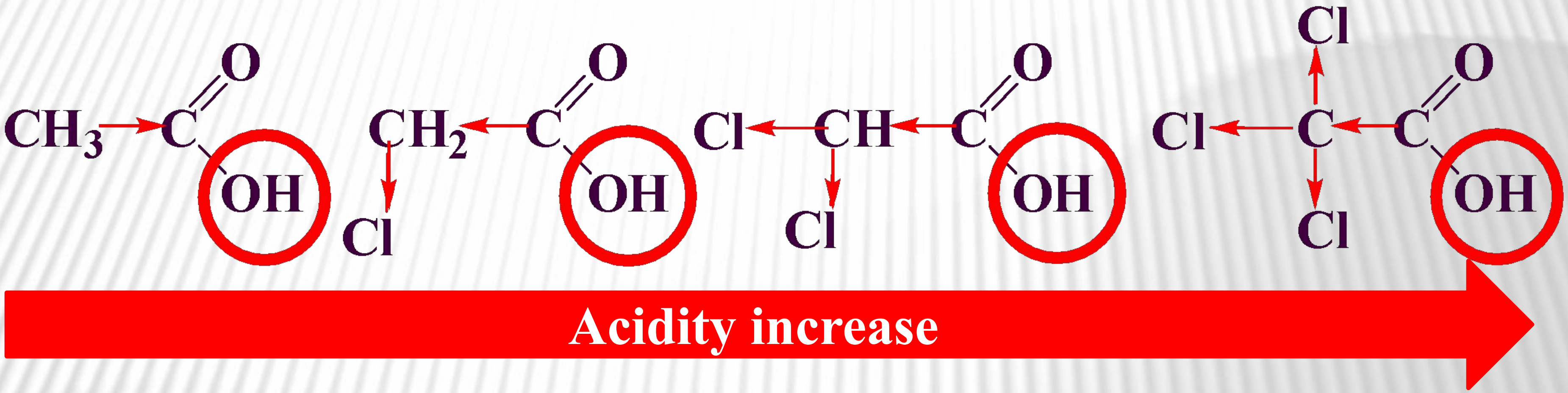
Atomic size increase

CH NH OH SH

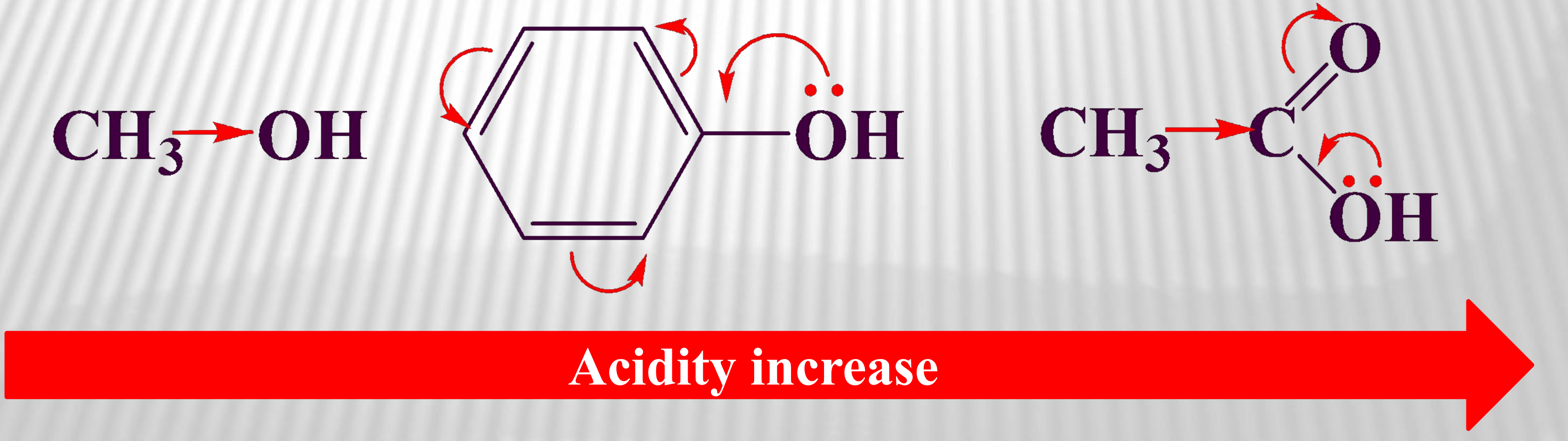
Acidity increase

The influence of substituents effects

- **inductive effect**



- **mesomeric effect**

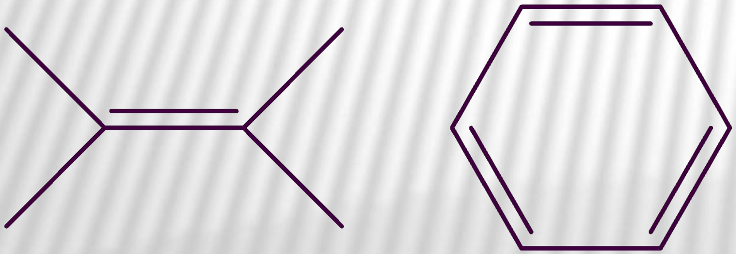


Comparison the basicity

The more stable is an cation and the more available a lone-pair of electrons, the stronger is an base!

The factors which influence the stability of conjugate acids is the same but they act in the opposite direction:

***π*-bases** → **Basicity increase** → ***n*-bases**



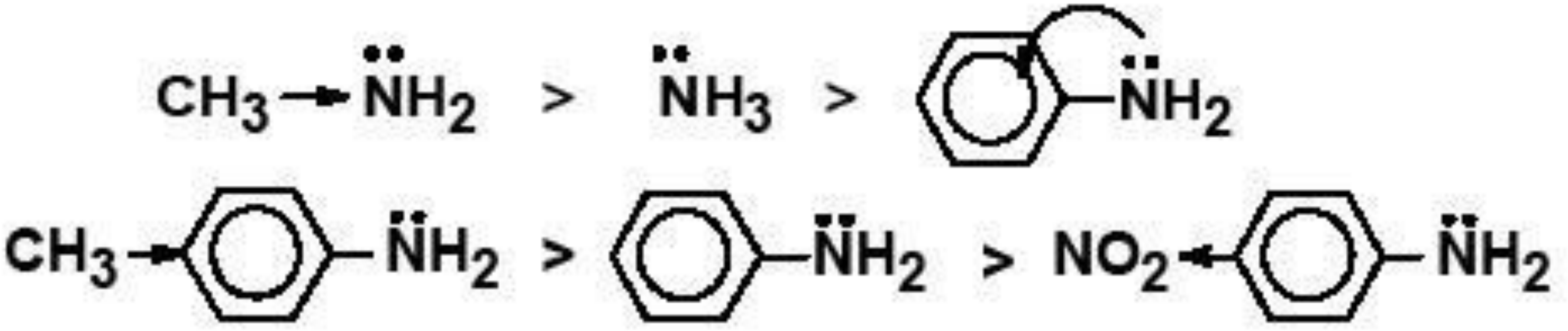
$R\ddot{N}H_2$ $R\ddot{O}H$ $R\ddot{S}H$

The influence of atom nature in the basic site

S **O** **N**

Basicity increase

The influence of substituents effects



Lewis concept

A Lewis acid **is any substance that can accept an electron pair in forming a covalent bond.**

A Lewis base **is any substance that can donate an electron pair in forming a covalent bond.**

$$(CH_3)_3N: + BF_3 \quad = \quad (CH_3)_3N^+ - BF_3^-$$