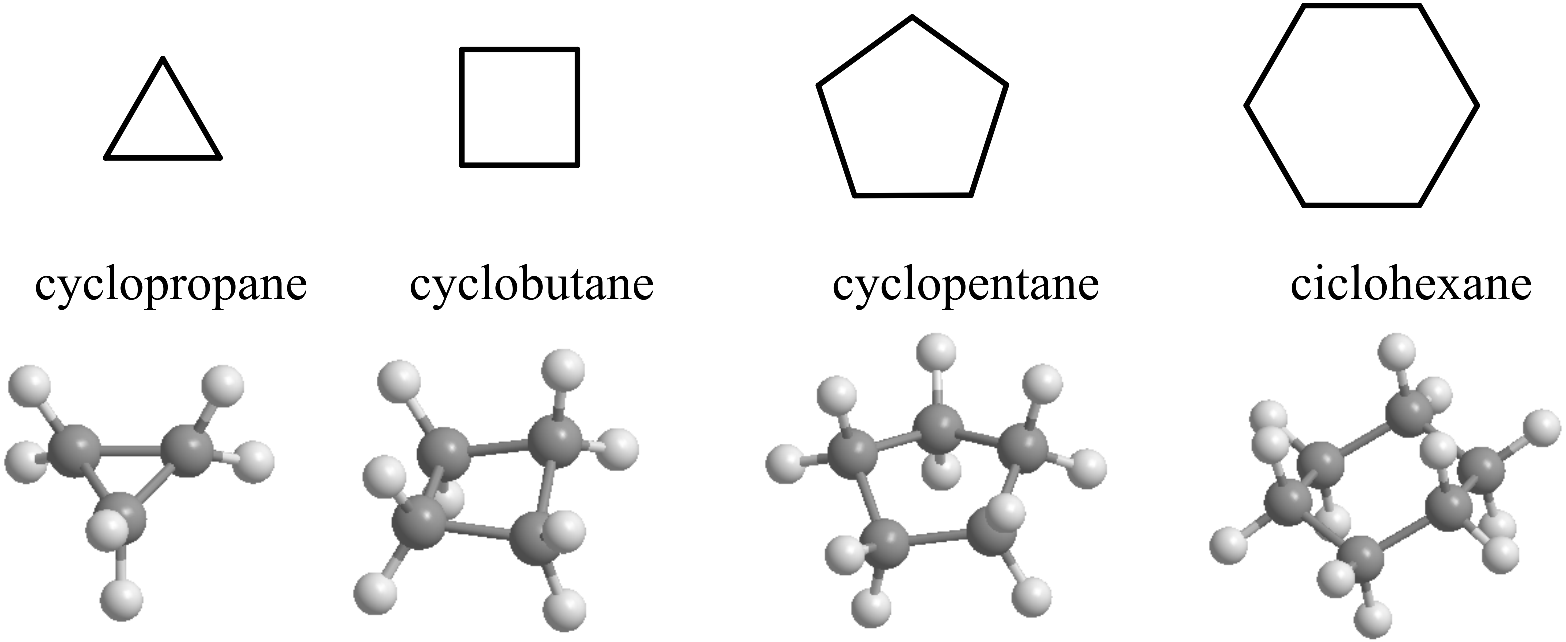
Cycloalkanes(C_nH_{2n})

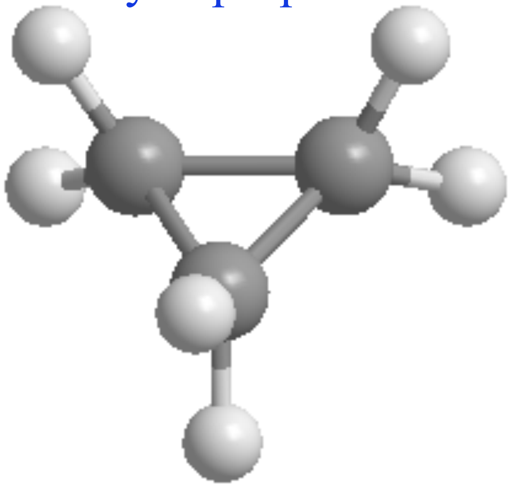
Cycloalkanes are cyclic saturated hydrocarbons



They can give addition reactions that cause the ring to break and the formation of open chain compounds. The unusual fact that an alkane gives addition reactions is possible as cycloalkanes have a so-called ring tension.

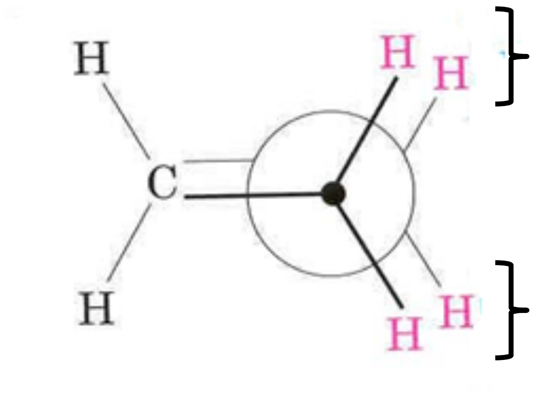
- for an sp^3 carbon, any deviation from a tetrahedral angle is accompanied by an angular strain.
- each pair of sp^3 carbon atoms tends to "arrange" and "maintain" their bonds offset relative to each other (staggered): any deviation from such an arrangement involves a torsional strain.
- a steric tension is also present due to the *steric hindrance* between neighboring groups

cyclopropane



a single conformation: planar

In cyclopropane, bond angles of 60 ° cause a very large angular tension.
In this conformation there are 6 pairs of interactions due to eclipsed C-H bonds



eclipsed hydrogens

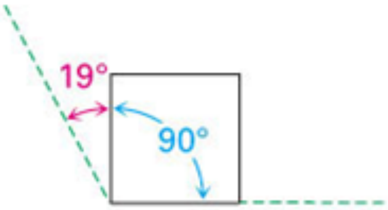
eclipsed hydrogens

Angular strain: the strain that arises from the expansion or compression of the bond angles.

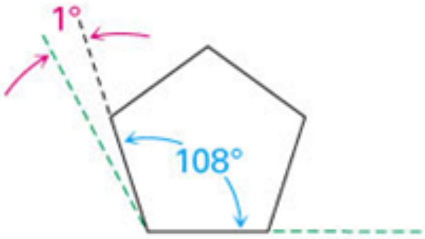
Torsional strain: the strain caused by the eclipsing of bonds on adjacent atoms.

Steric strain: the strain caused by the repulsive interactions between atoms that are too close to each other

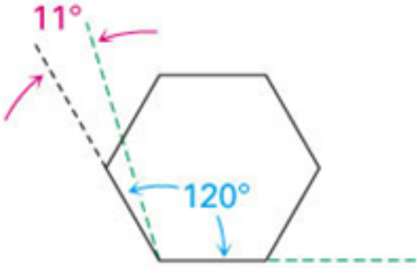
cyclopropane



cyclobutane



cyclopentane



cyclohexane

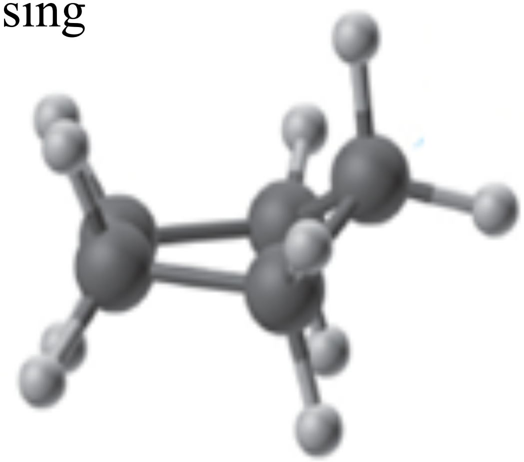
Cycloalkanes partially solve the problem of annular tension by adopting non-planar conformations

In the planar conformation of cyclopentane there are as many as 10 pairs of interactions due to eclipsed C-H bonds

The folding partially eliminates the torsional tension due to the eclipsing

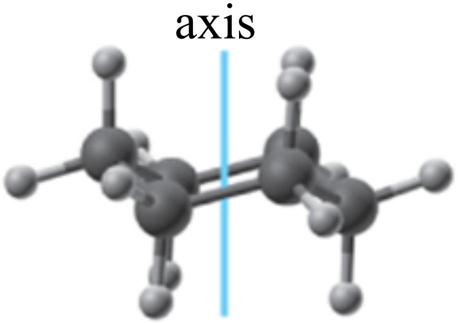
cyclopentane

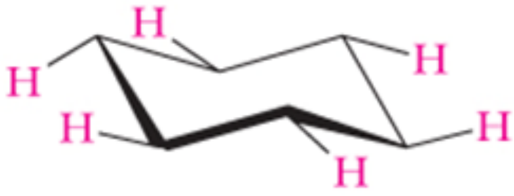
planar conformation



envelope conformation

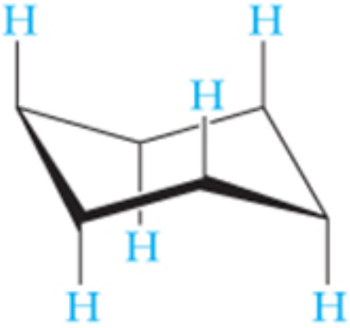
Cycloalkanes partially solve the problem of annular strain by adopting non-planar conformations



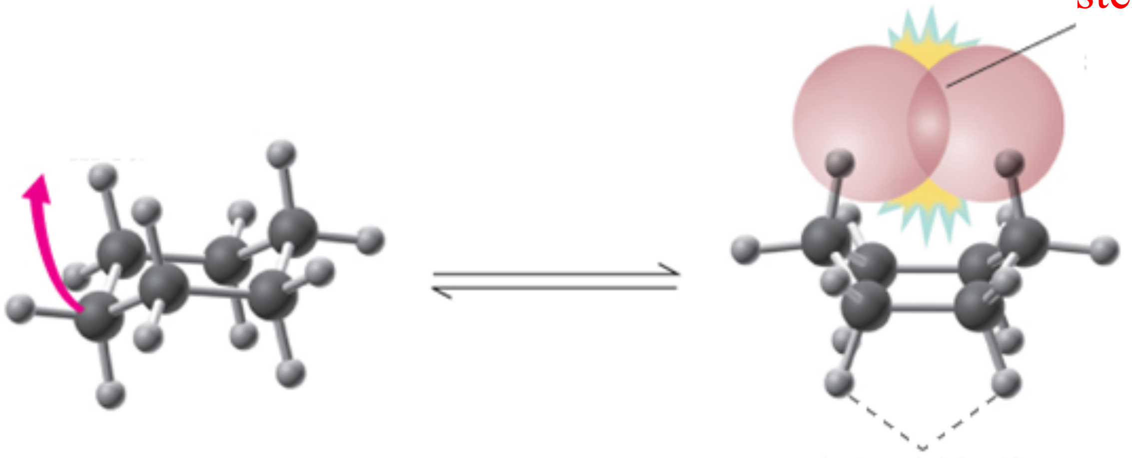


6 equatorial C-H

6 axial C-H



The chair conformation is the most stable because it is free from torsional stresses given by the staggered arrangement of the bonds of each carbon-carbon pair and has less steric repulsion.



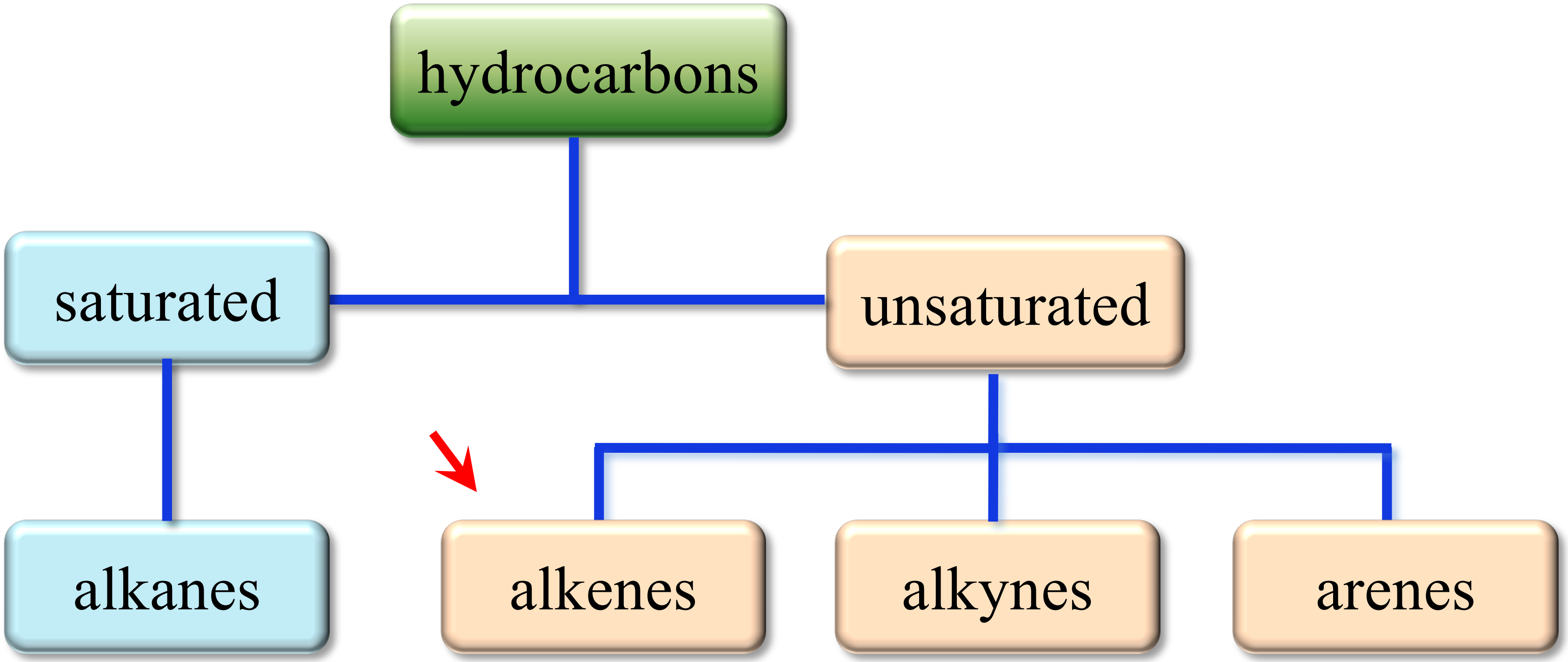
steric clash

chair confromation

boat conformation

interaction between eclipsed Hs

Classification of hydrocarbons



hydrocarbons

saturated

unsaturated

alkanes

alkenes

alkynes

arenes

only C-C single bons (σ)

H_3C-CH_3

ethane

sp³ orbitals

a double bond (σ & π)

$H_2C=CH_2$

ethene

sp² orbitals

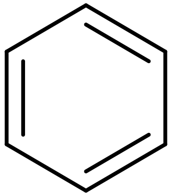
a triple bond (σ & π)

$HC\equiv CH$

ethin

sp orbitals

1 or more benzene rings

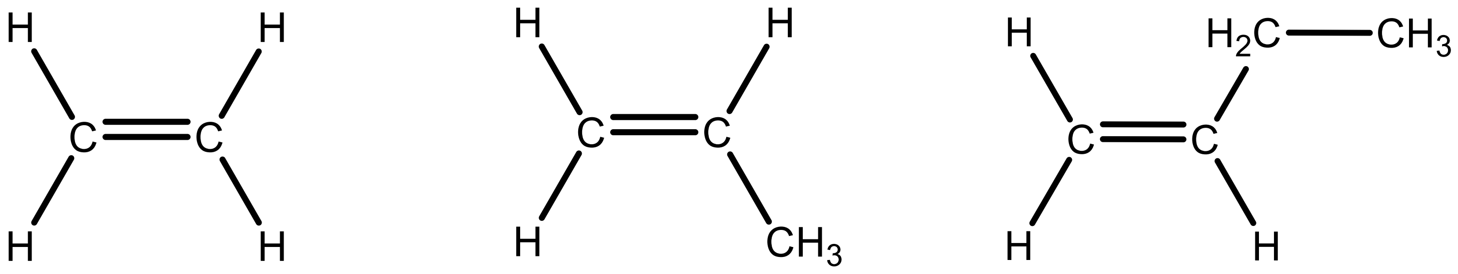


benzene

sp² orbitals

Alkenes (C_nH_{2n})

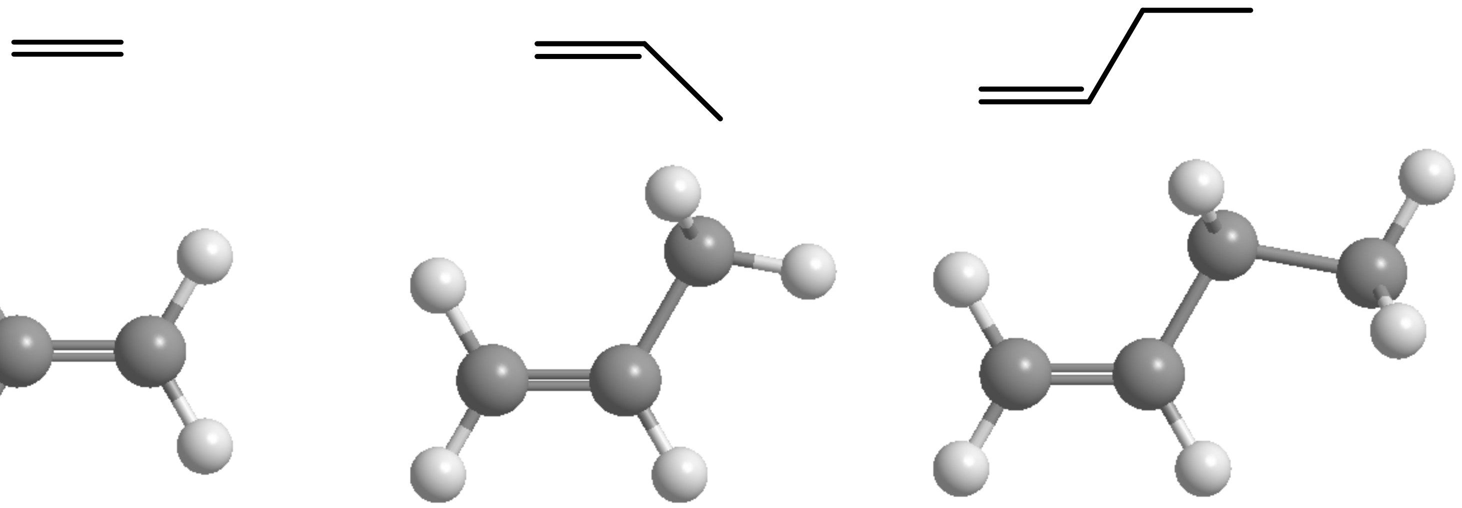
Alkenes are hydrocarbons characterized by the presence of a carbon-carbon double bond (σ + π). The distinctive suffix of the series is -ene



ethylene

propylene

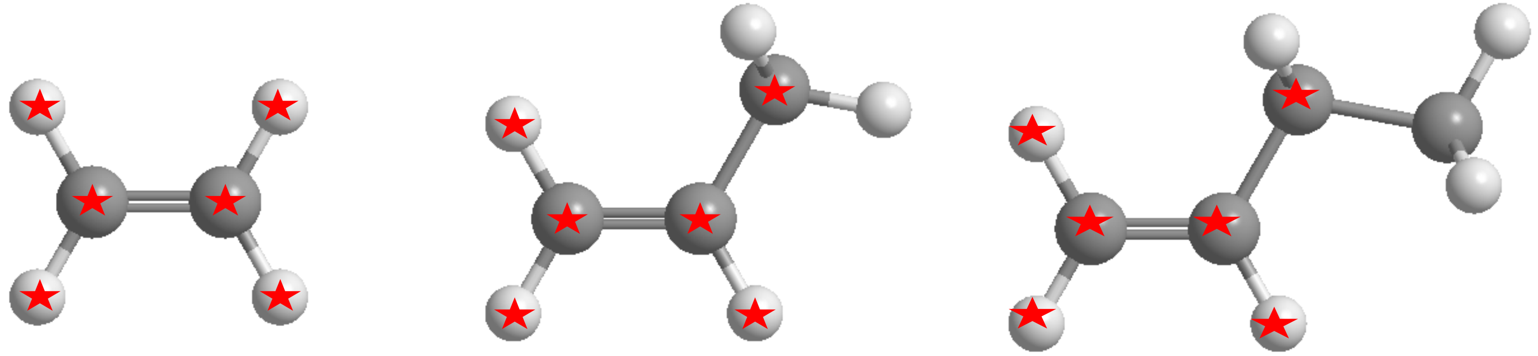
1-butene



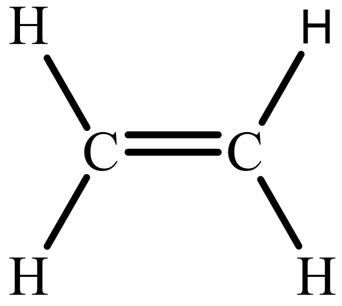
- The carbon-carbon double bond is formed by an σ bond (bond energy ca. 347 kJ / mol), resulting from the superposition of two **sp**^{2} orbitals of the two carbon atoms and a π bond (bond energy ca. 260 kJ / mol), given by the superposition of the two **p** orbitals.

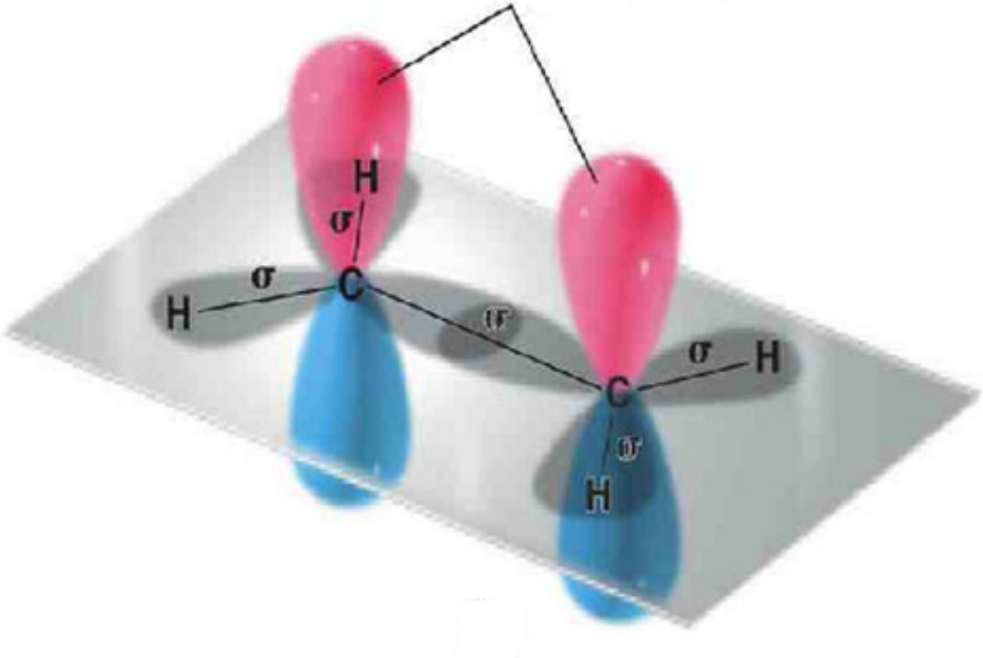
- The double bond is therefore stronger than a simple bond (607 vs 350 kJ / mol) and the bond distance is shorter(1.34 vs 1.53 Å).

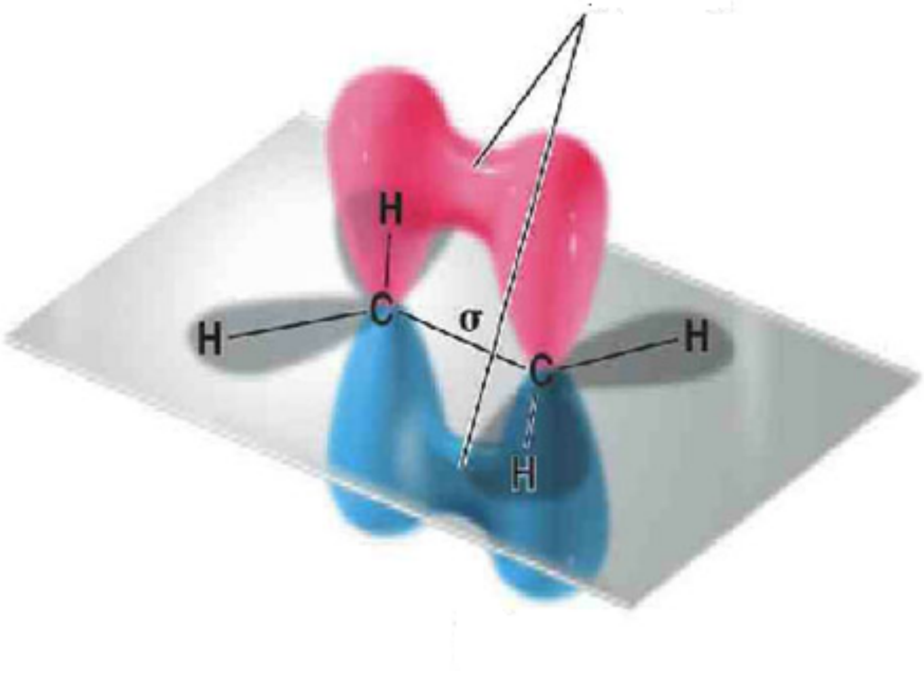
- In the portion of the molecule that contains the double bond, 6 atoms lie in the same plane (★)



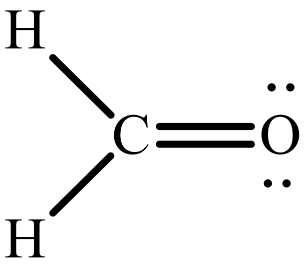
Ethene (o ethylene)



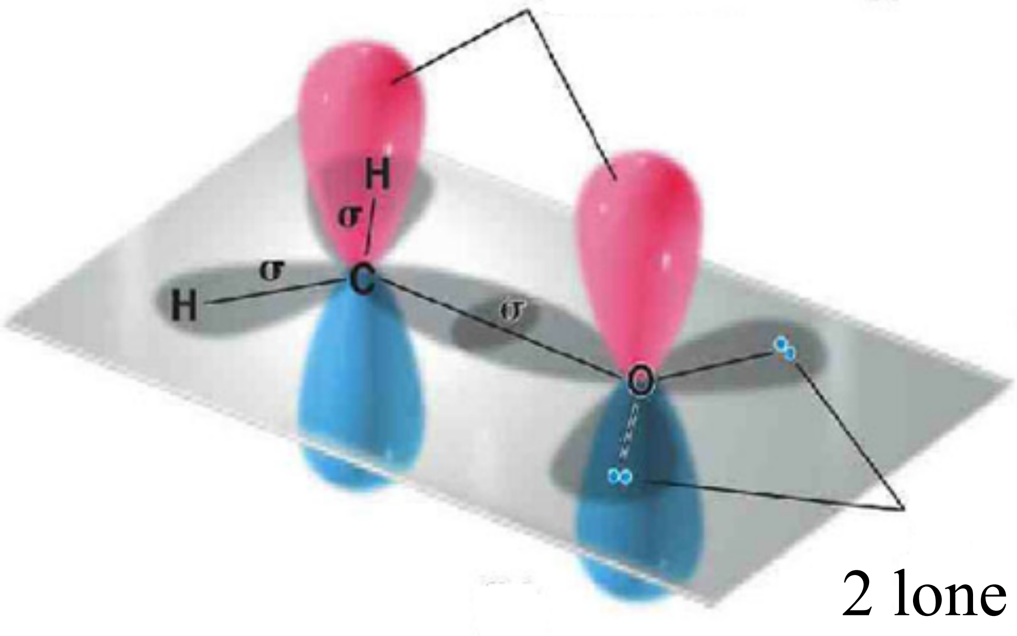

2p orbitals


π bond

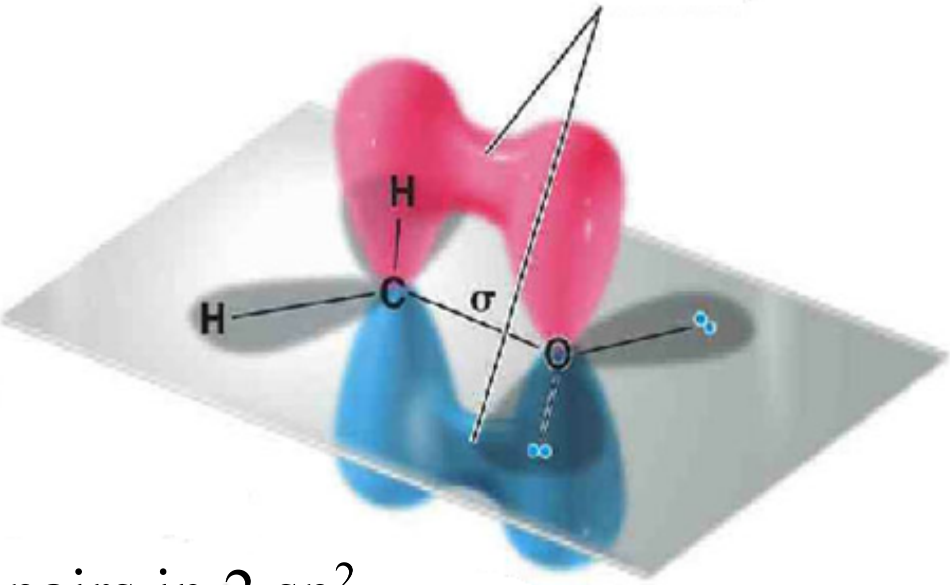
formaldehyde



2p orbitals



π bond



2 lone pairs in 2 sp^2
hybrid oxygen orbitals

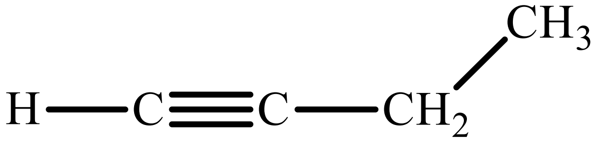
In alkynes (C_2H_{2n-2}) there are 2 π bonds

$H-C\equiv C-H$

ethin (acetylene)

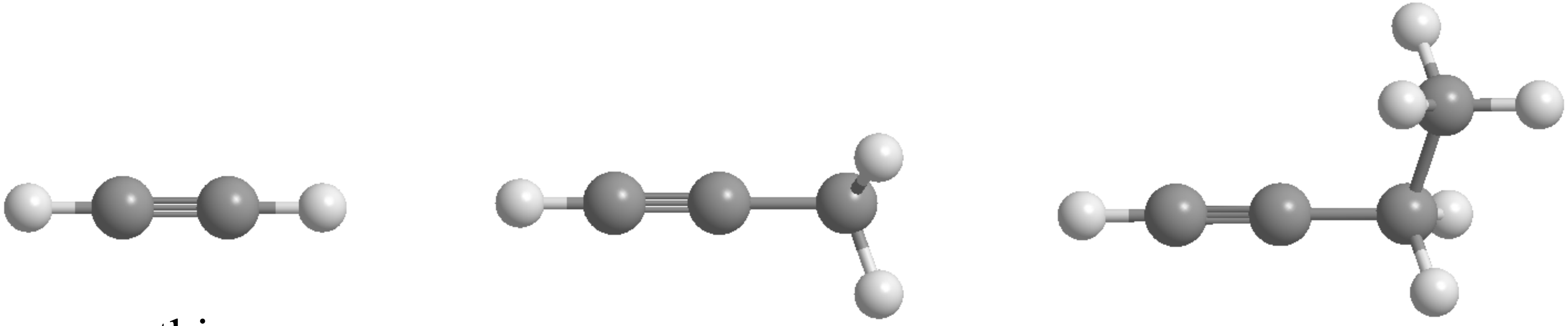
$H-C\equiv C-CH_3$

propyne

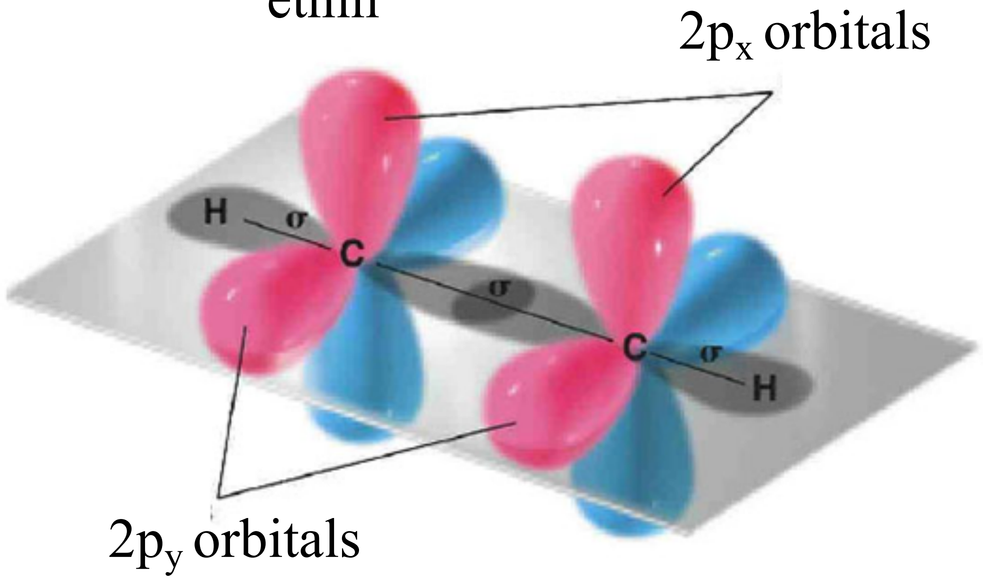


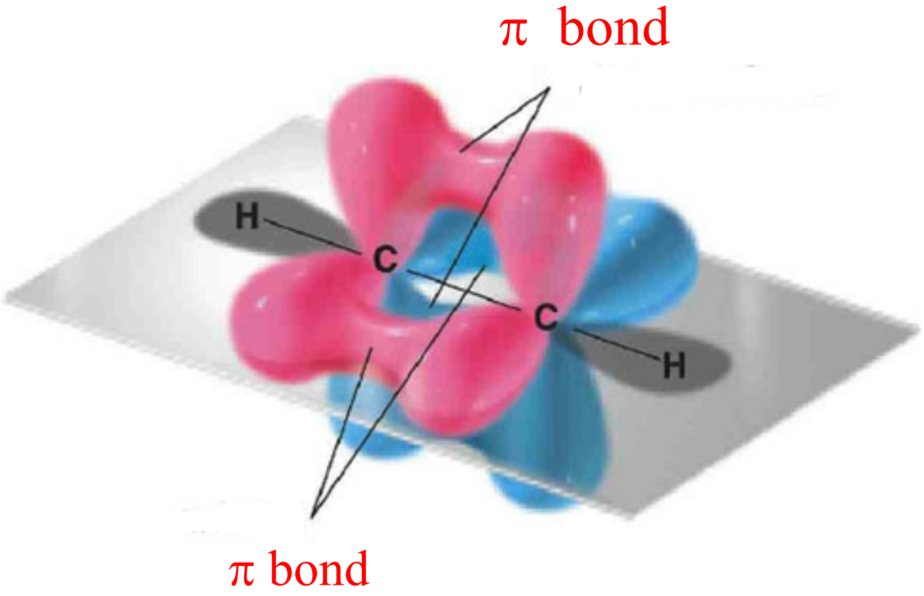
$H-C\equiv C-CH_2-CH_3$

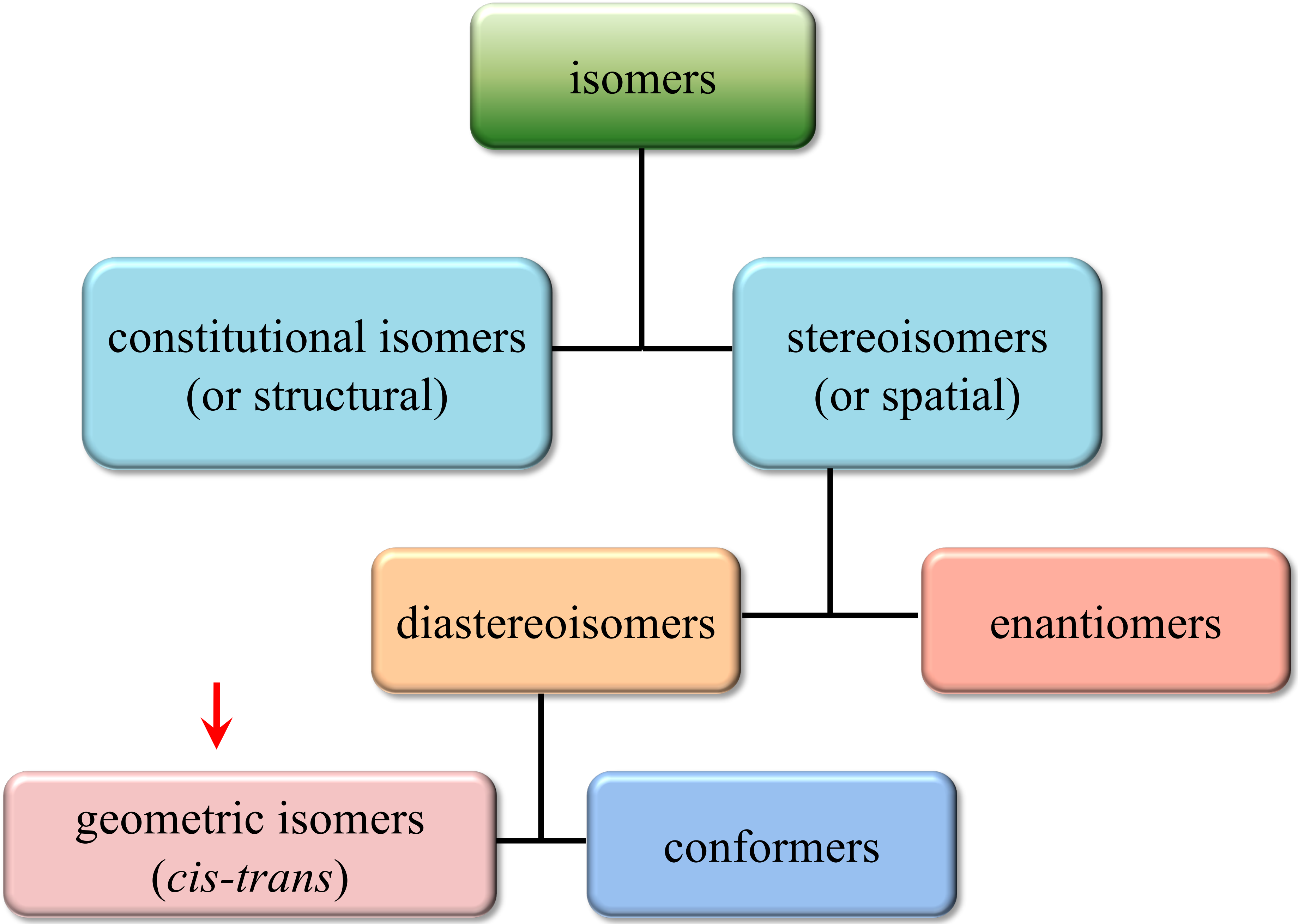
butyne



ethin







isomers

constitutional isomers (or structural)

stereoisomers (or spatial)

diastereoisomers

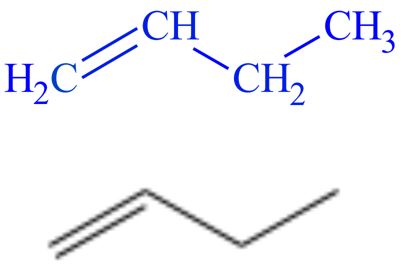
enantiomers

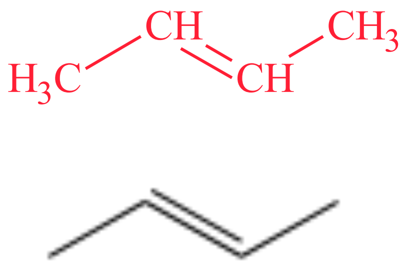
geometric isomers (*cis-trans*)

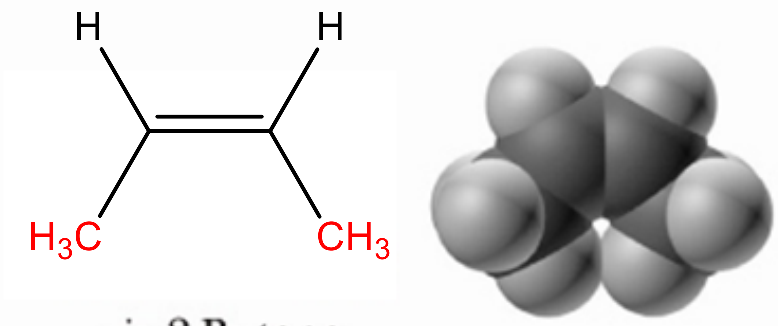
conformers

Geometric isomerism

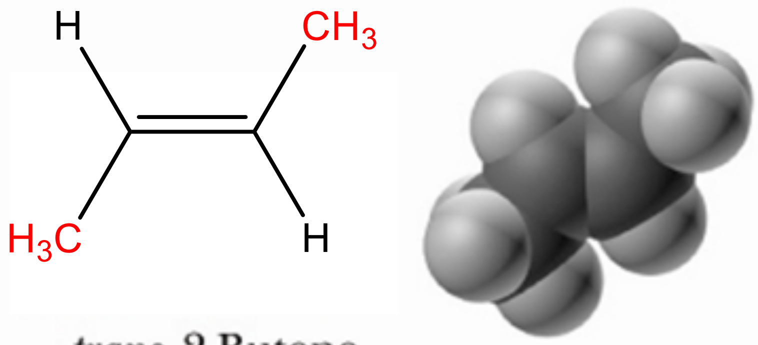
Depending on the position of the double bond, butene can exist as 1-butene or 2-butene; 2-butene can in turn have two different structures:







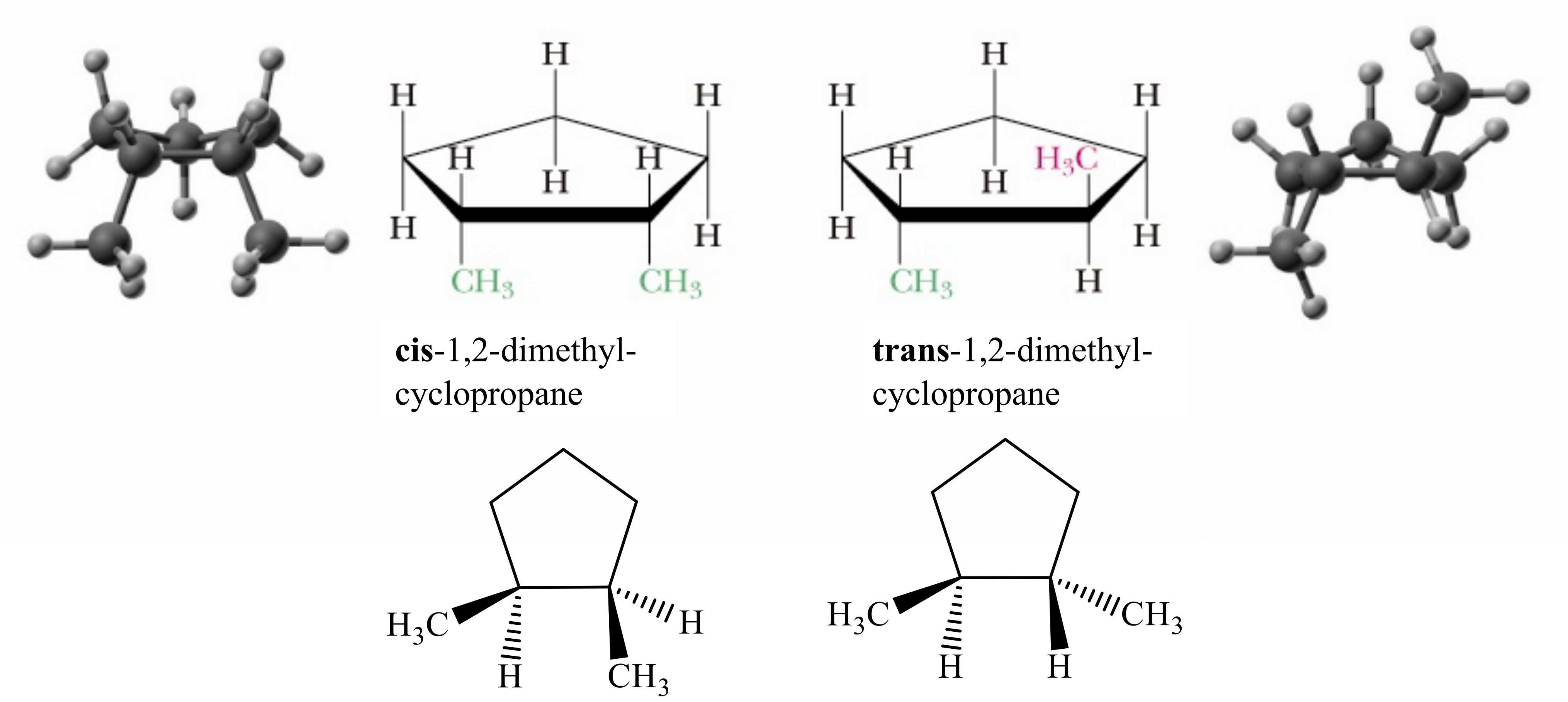
cis-2-Butene
pf – 139°C, pc 4°C



trans-2-Butene
pf – 106°C, pc 1°C

Stereoisomers: they differ only in the spatial arrangement of the atoms. More precisely, they are diastereomers because they are not the mirror image of each other (they are not enantiomers).

Cis-trans geometric isomerism is also present if a simple C-C bond cannot rotate, therefore also in cyclic hydrocarbons



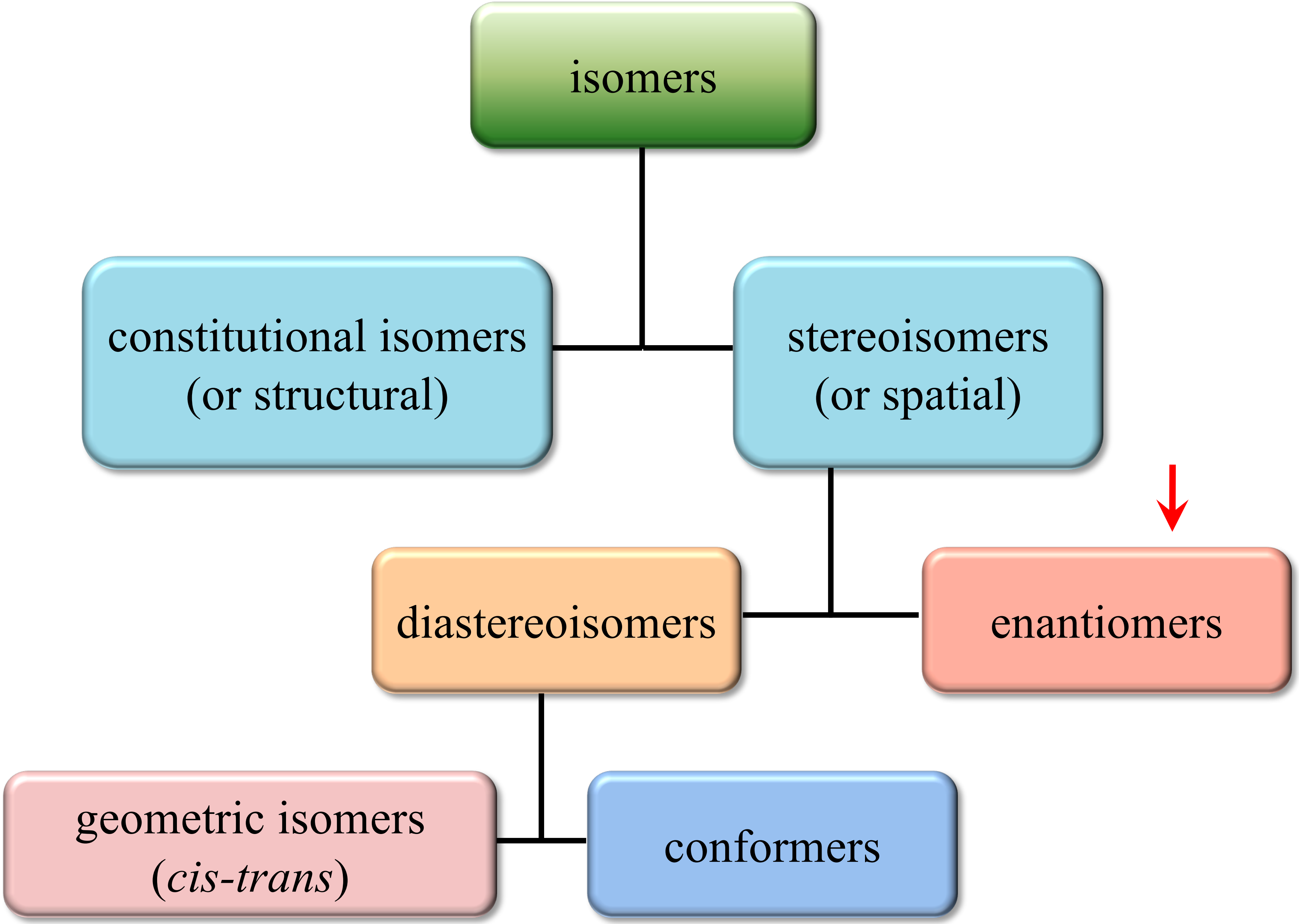
cis-1,2-dimethyl-cyclopropane

trans-1,2-dimethyl-cyclopropane

Bond length and energy in some aliphatic hydrocarbons

compound	formula	bond	OS*	bond length(Å)	bond energy (kJ/mol)
ethane	C_2H_6	C-C	sp^3–sp^3	1.53	376
		C-H	sp^3–1s	1.11	422
ethene	C_2H_4	C-C	sp^2–sp^2	1.34	727
		C-H	sp^2–1s	1.10	464
ethin	C_2H_2	C-C	sp–sp	1.21	966
		C-H	sp–1s	1.09	556

* OS = orbital superposition; in the case of ethene and ethin π are not indicated



isomers

constitutional isomers
(or structural)

stereoisomers
(or spatial)

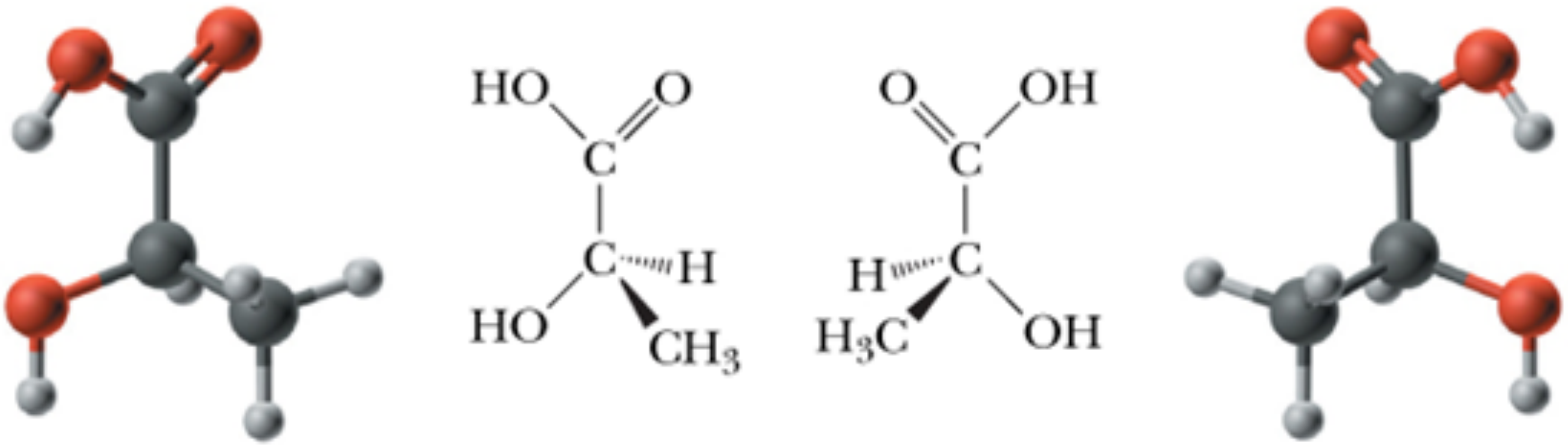
diastereoisomers

enantiomers

geometric isomers
(*cis-trans*)

conformers

Optical isomerism and molecular chirality

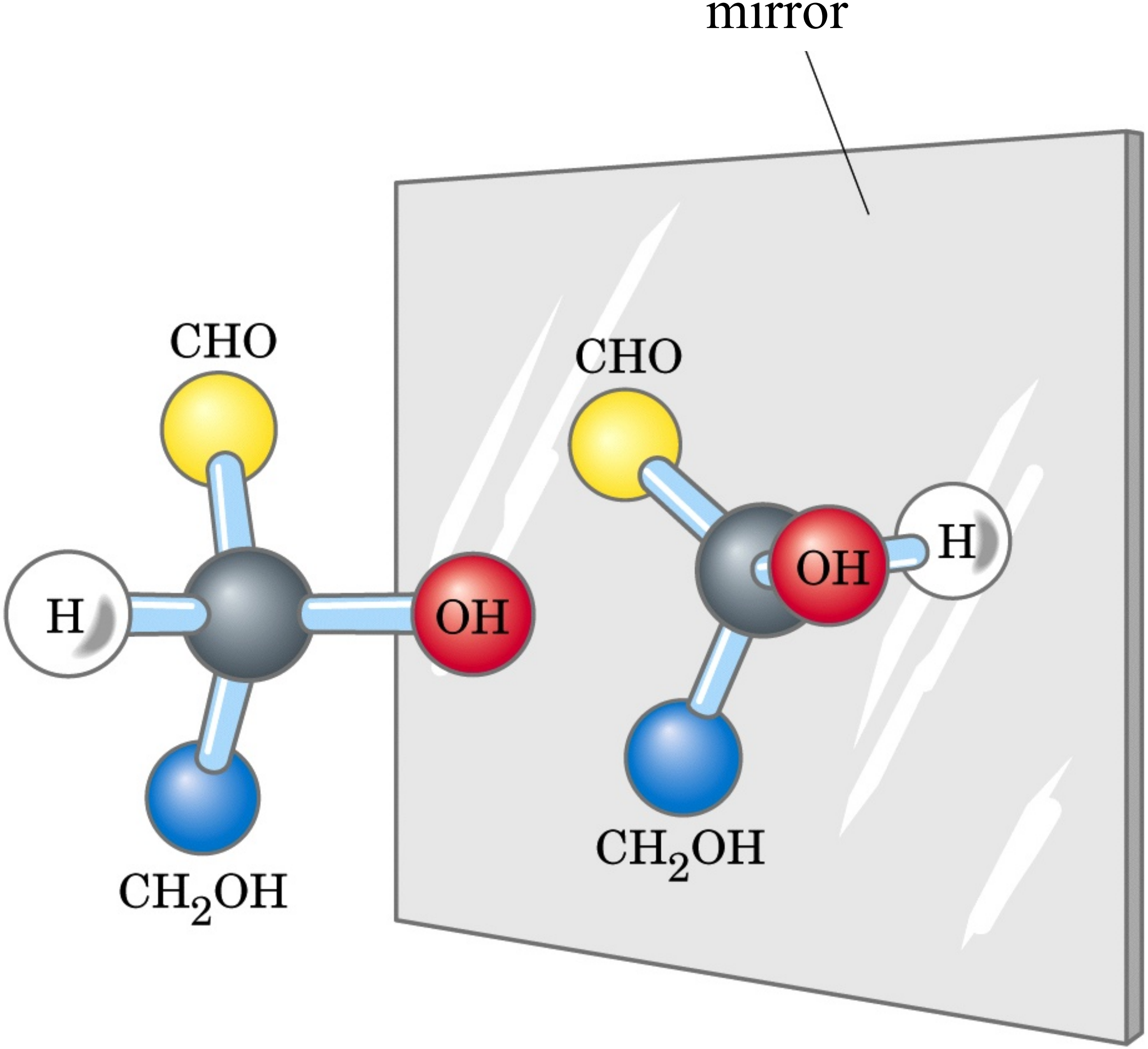


Lactic acid

- these two molecules differ only in that one is the non-superimposable mirror image of the other

- two stereoisomers which are one the non-superimposable mirror image of the other are called enantiomers. This property is called chirality

- enantiomers have the same physical and chemical properties except one particular optical property: the direction of rotation of the plane of polarized light


mirror
CHO
H
OH
CH₂OH
CHO
OH
H
CH₂OH

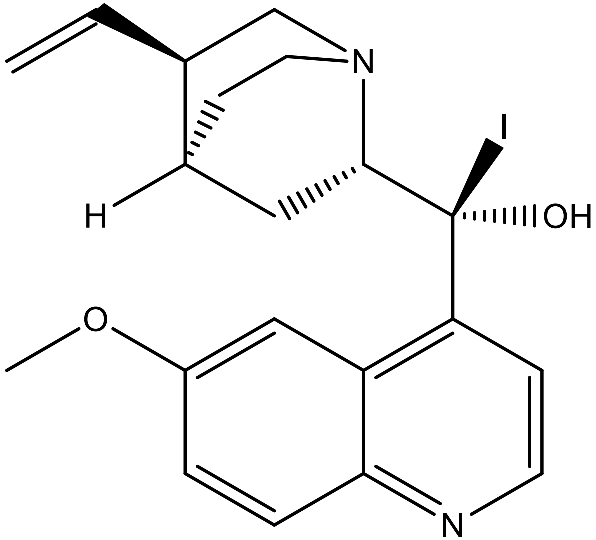
Polarizing filter in photography

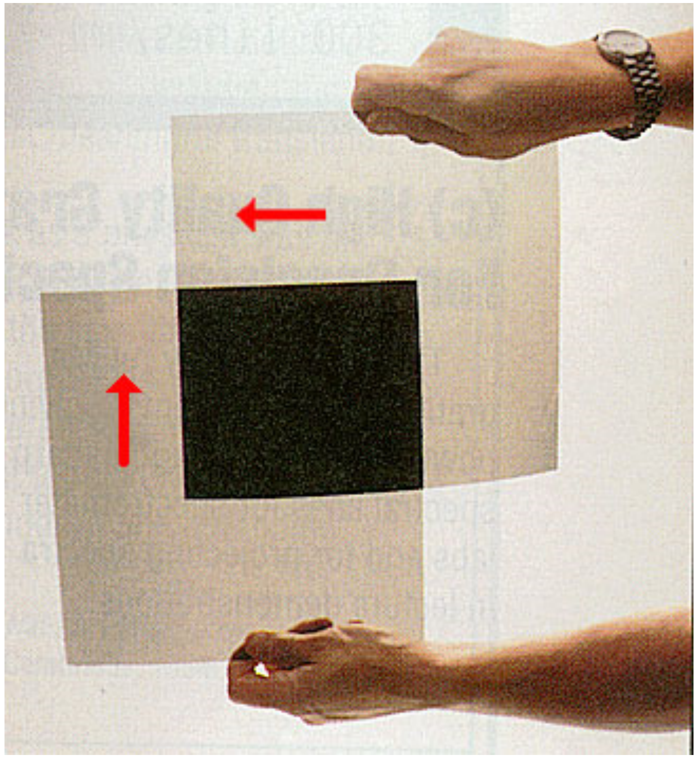
The filter mounted on the camera can be rotated until the reflection is eliminated

Polarizers

- Calcite crystals ($CaCO_3$)
- Polaroid: series of microscopic iodoquinine sulphate crystals layered on a transparent polymeric nitrocellulose film.

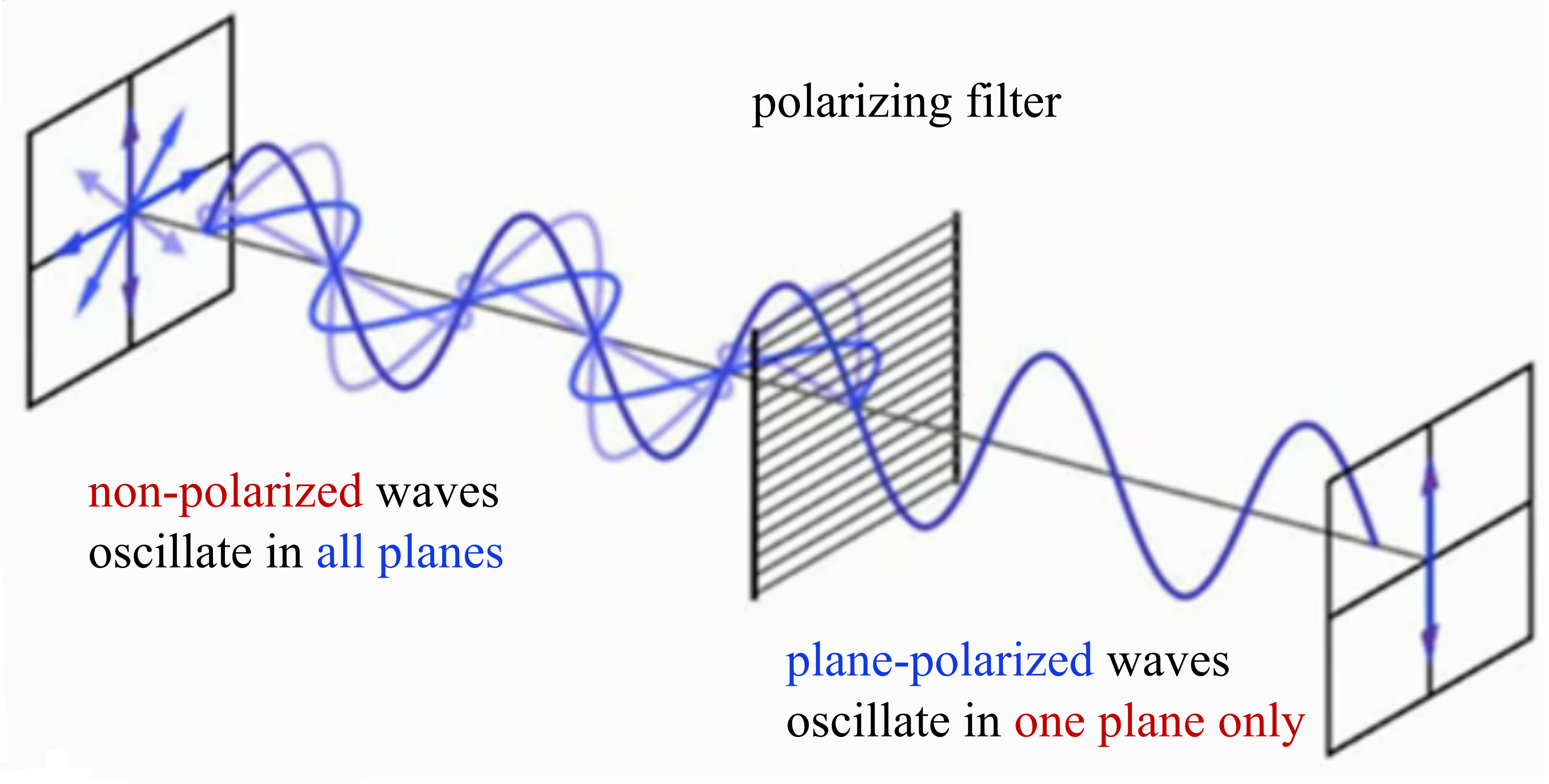
During the manufacturing process the needle-like crystals are aligned by applying a magnetic field. This sheet is dichroic: it tends to absorb polarized light perpendicular to the direction of alignment of the crystals, letting the light pass parallel to them.





Polarized light

Light source

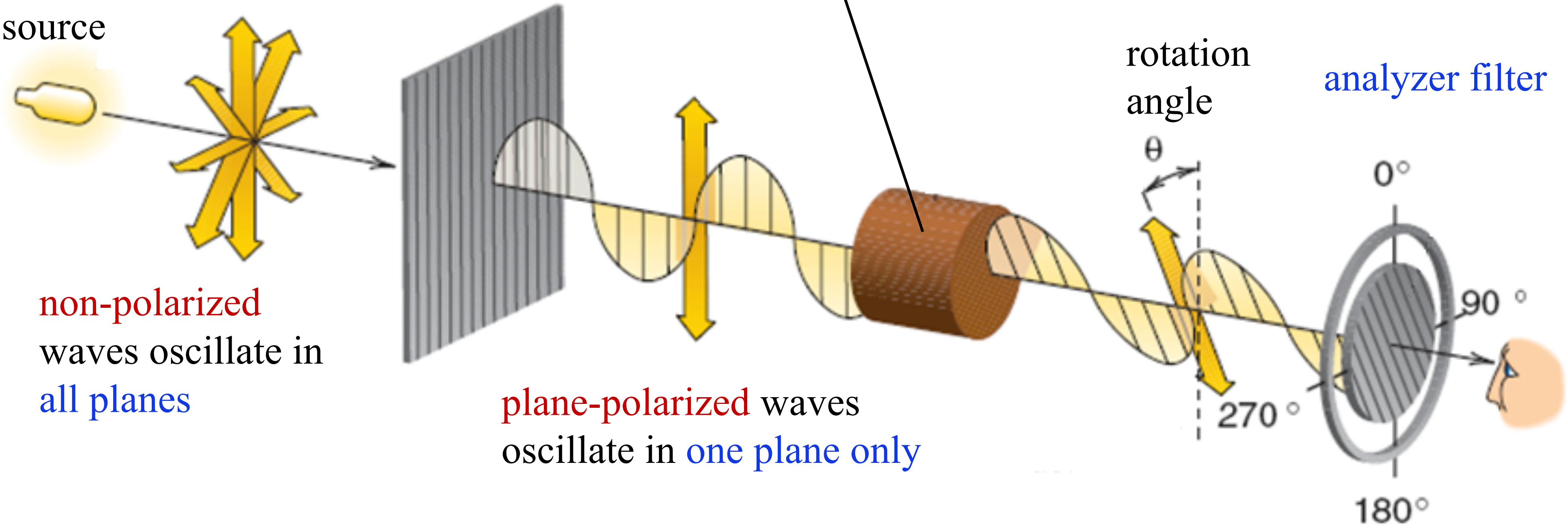


polarizing filter

non-polarized waves oscillate in all planes

plane-polarized waves oscillate in one plane only

Chiral compounds rotate the plane of polarized light



Light source

polarizing filter

tube containing a solution of an optically active substance

rotation angle

analyzer filter

non-polarized waves oscillate in all planes

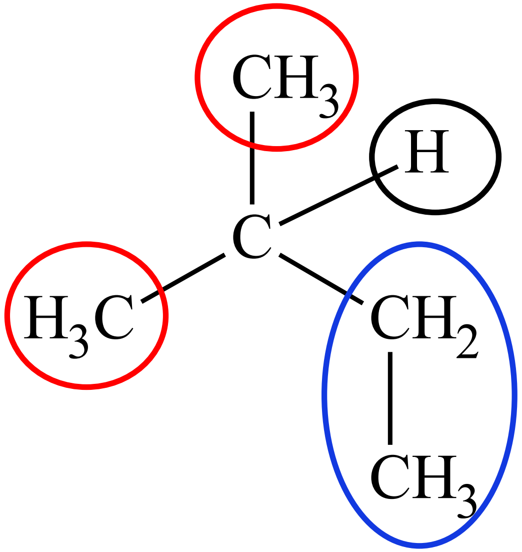
plane-polarized waves oscillate in one plane only

he optically active substance rotates the plane of polarized light by an angle θ

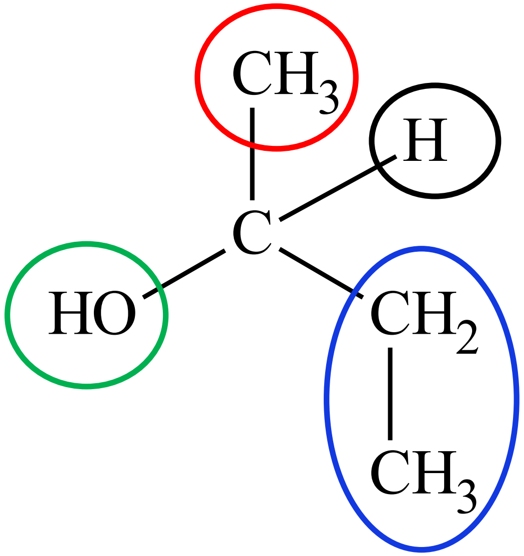
How is an optically active substance recognized?

If a compound contains an sp^3 carbon atom with 4 different substituents, then the compound will be optically active. This carbon is called asymmetric carbon.

Which of these two compounds is chiral?



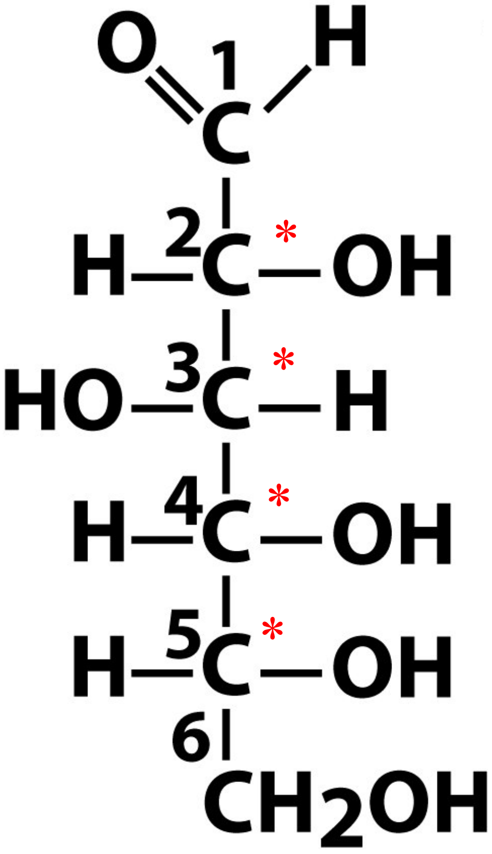
2-methyl-butane



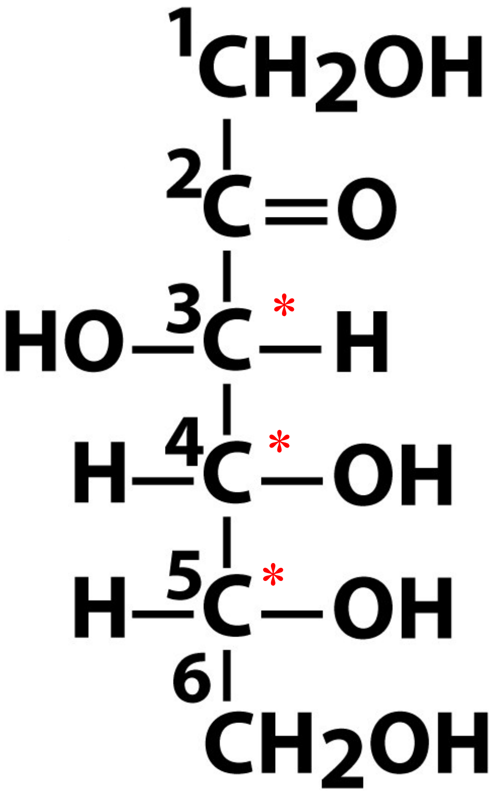
2-hydroxy-butane

it is chiral

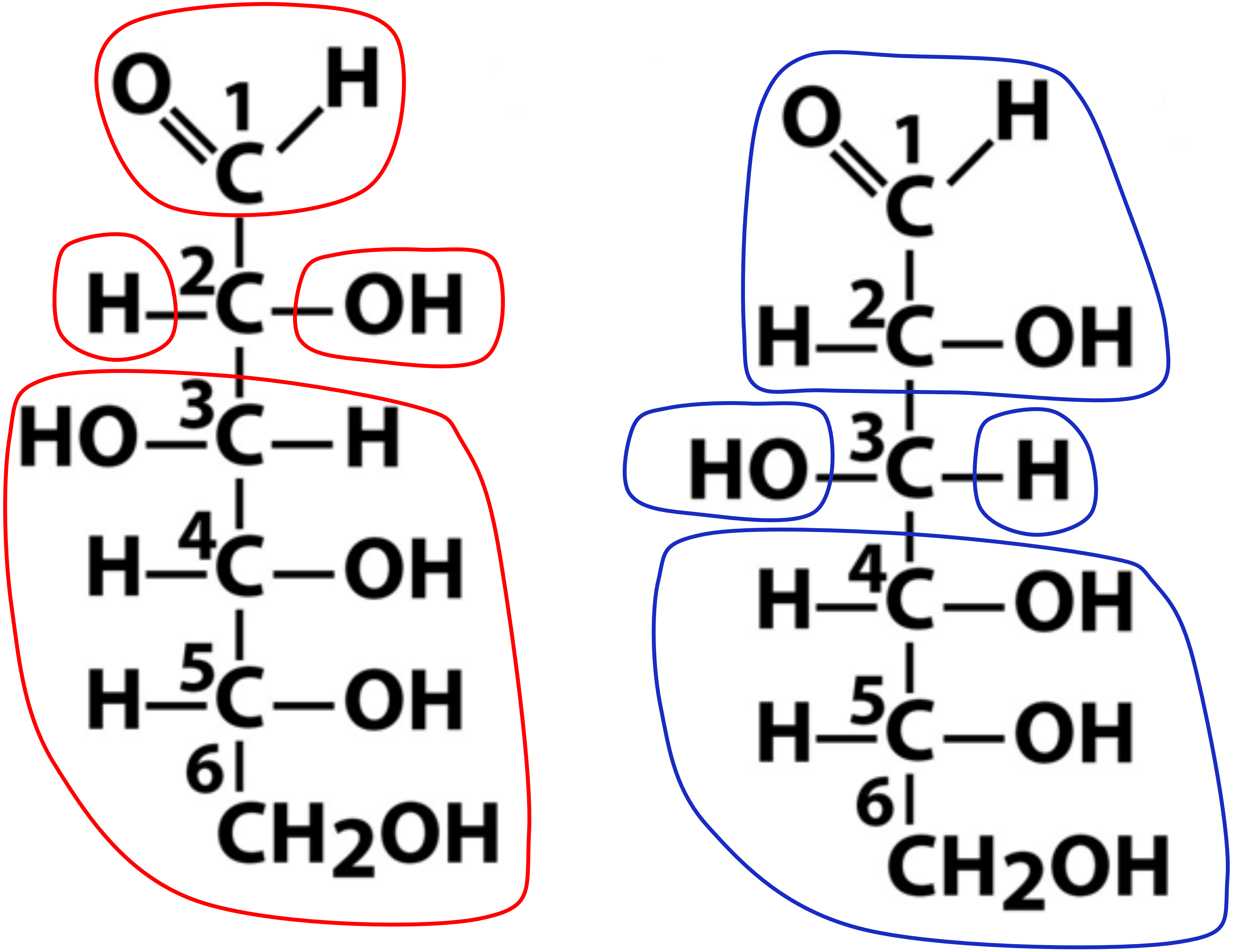
Many compounds contain more than one chiral center



D-glucose

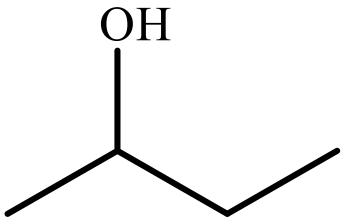


D-fructose

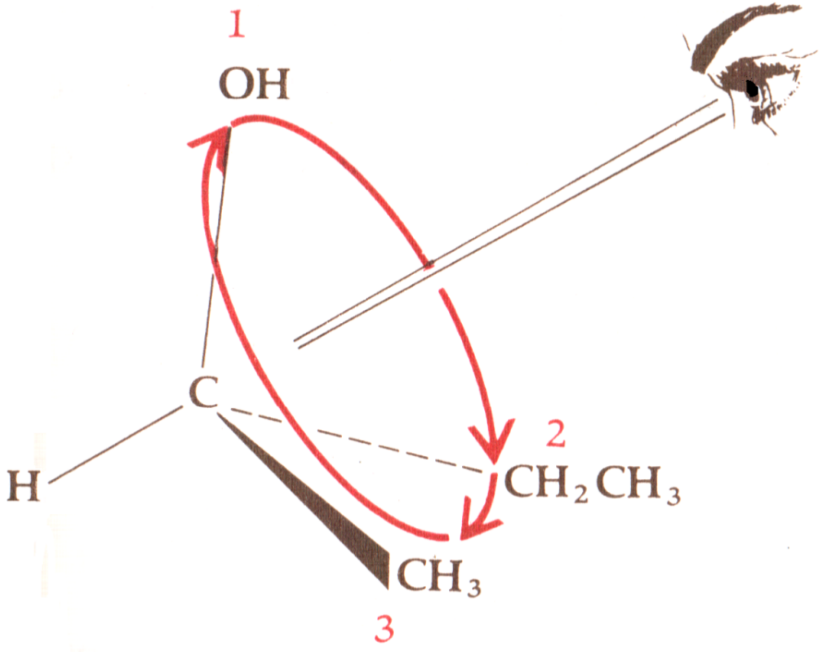

O
1
H
C
H
2
C
OH
HO
3
C
H
H
4
C
OH
H
5
C
OH
6
CH2OH
O
1
H
C
H
2
C
OH
HO
3
C
H
H
4
C
OH
H
5
C
OH
6
CH2OH

The Cahn-Ingold-Prelog system

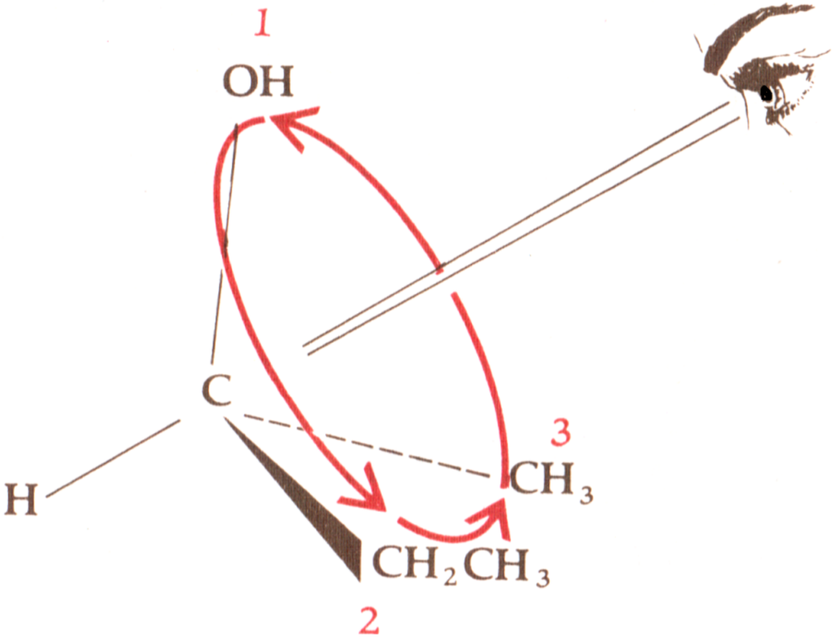
Priority: SH > OH > NH_2 > COOH > CHO > CH_2OH > C_6H_5 > ^2H > ^1H



2-butanol



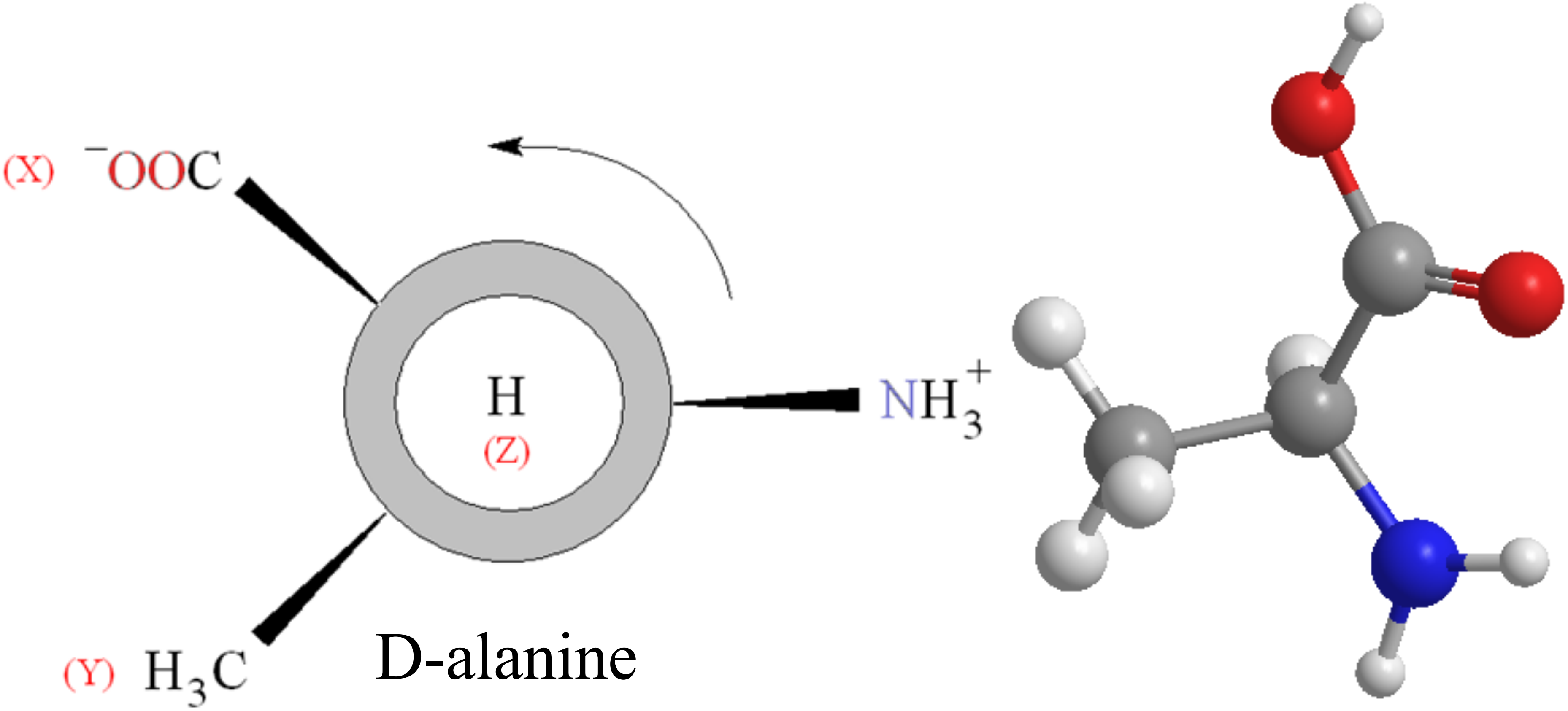
clockwise
D-2-butanol



counterclockwise
L-2-butanol

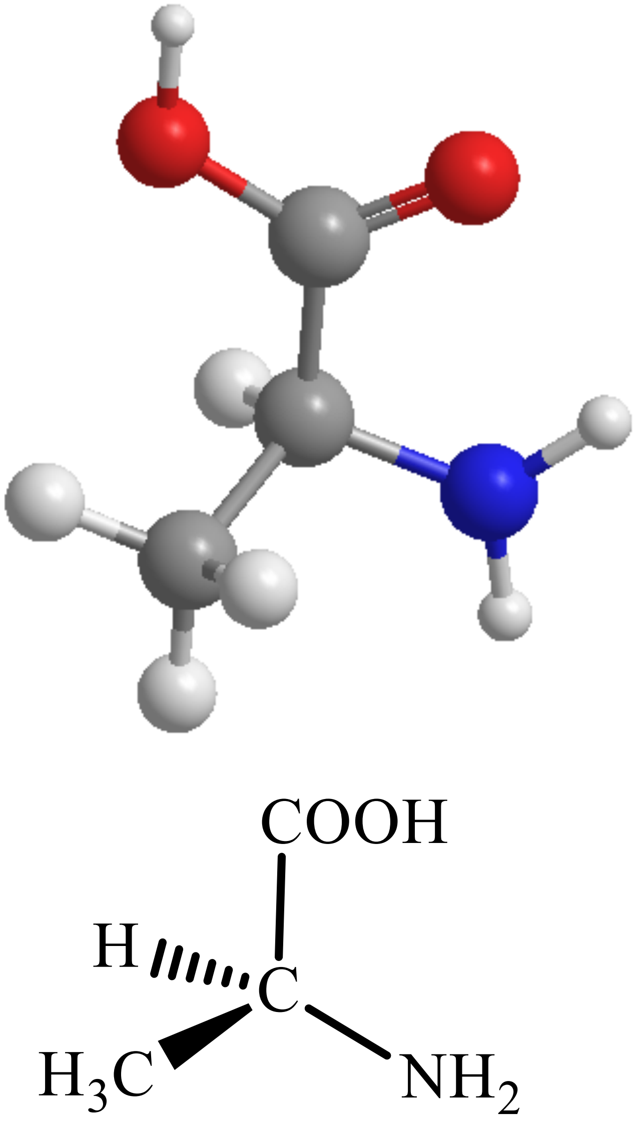
Il sistema Cahn-Ingold-Prelog

Priority: SH > OH > NH_2 > COOH > CHO > CH_2OH > C_6H_5 > ^2H > ^1H

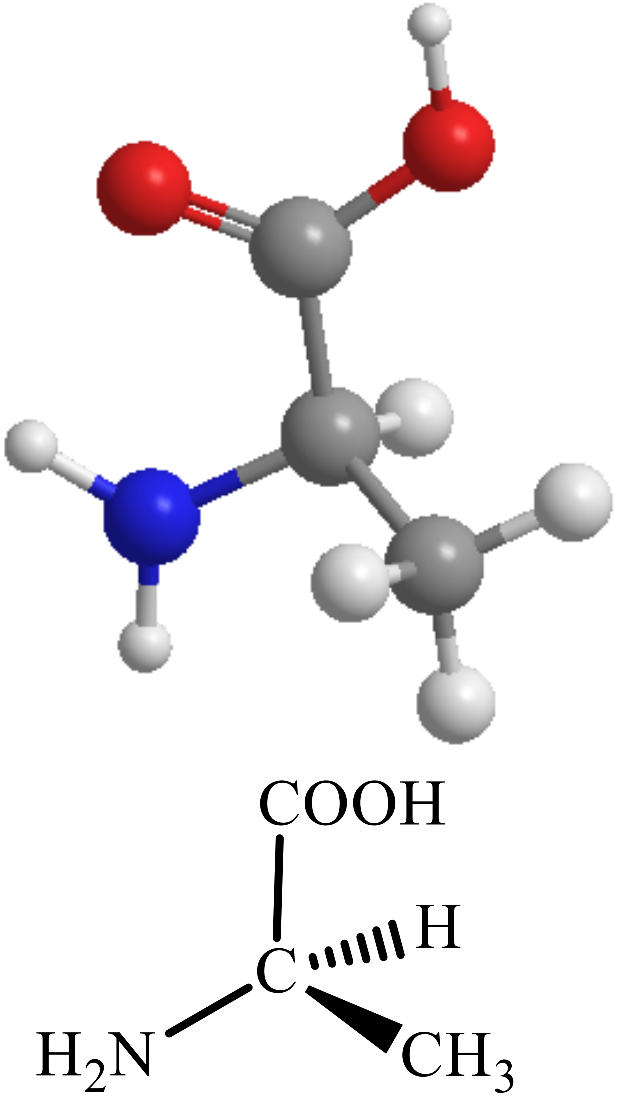


D-alanine

The stereoisomerism of amino acids

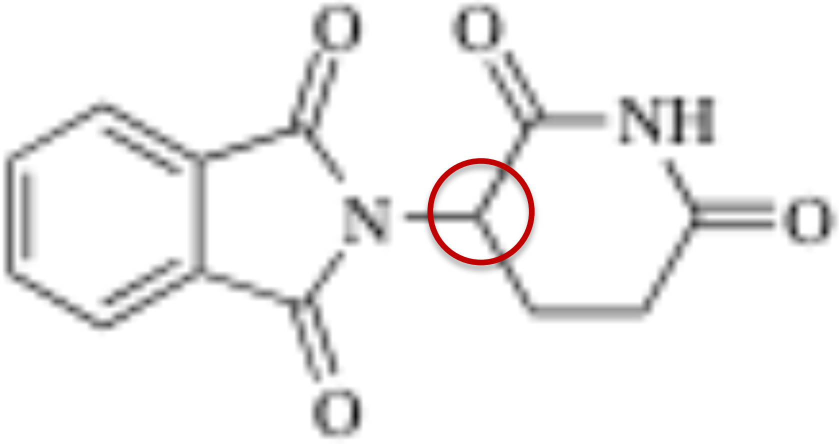


L-alanine



D-alanine

Thalidomide : there is a chiral center, where is it?



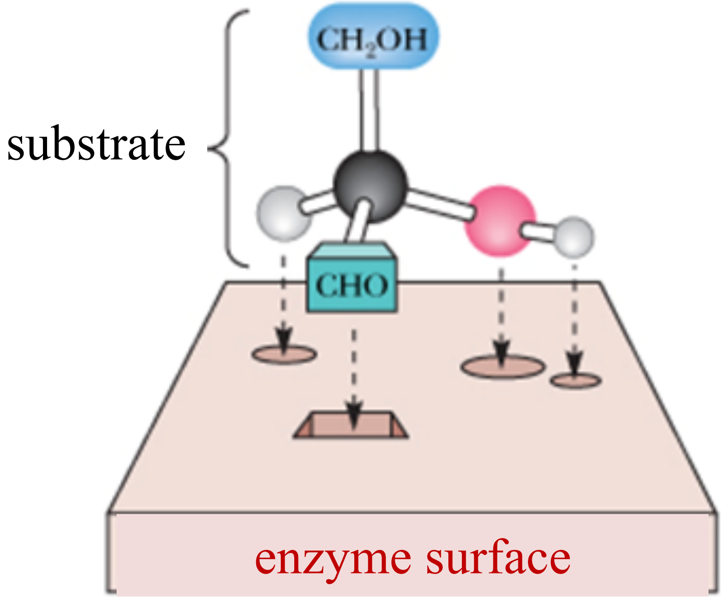
About 20,000 children affected

D-thalidomide

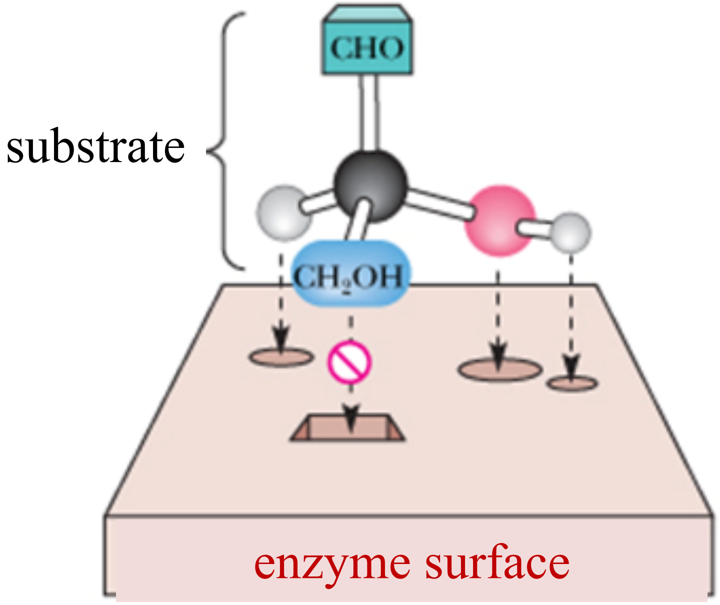
L-thalidomide

Enzymes are often highly stereospecific

Schematic diagram of the surface of an enzyme capable of interacting with D-glyceraldehyde in 3 binding sites and only in 2 of these sites with L-glyceraldehyde



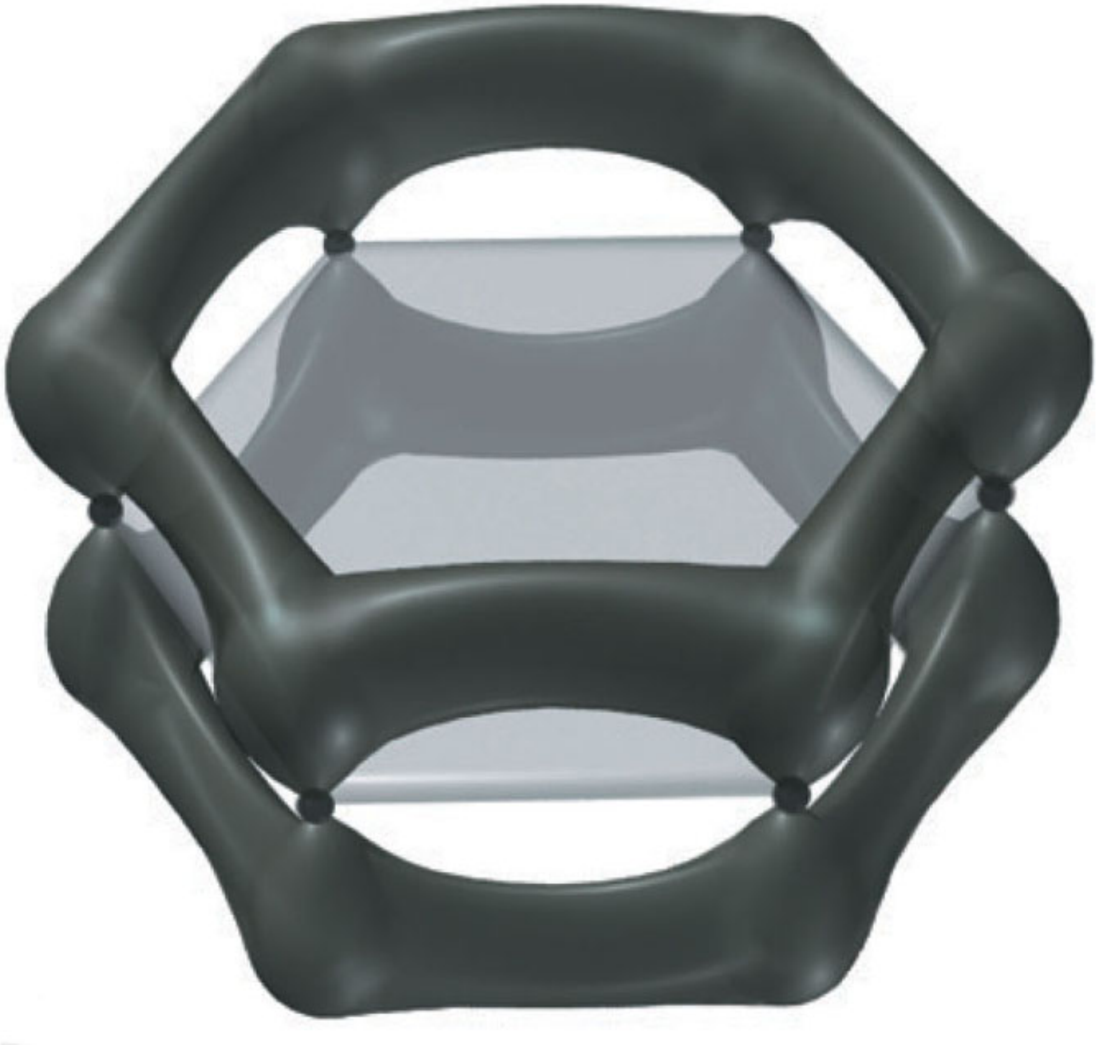
the D enantiomer adapts to 3 specific binding sites on the enzyme surface



the L enantiomer does not adapt to the same sites

le

Benzene



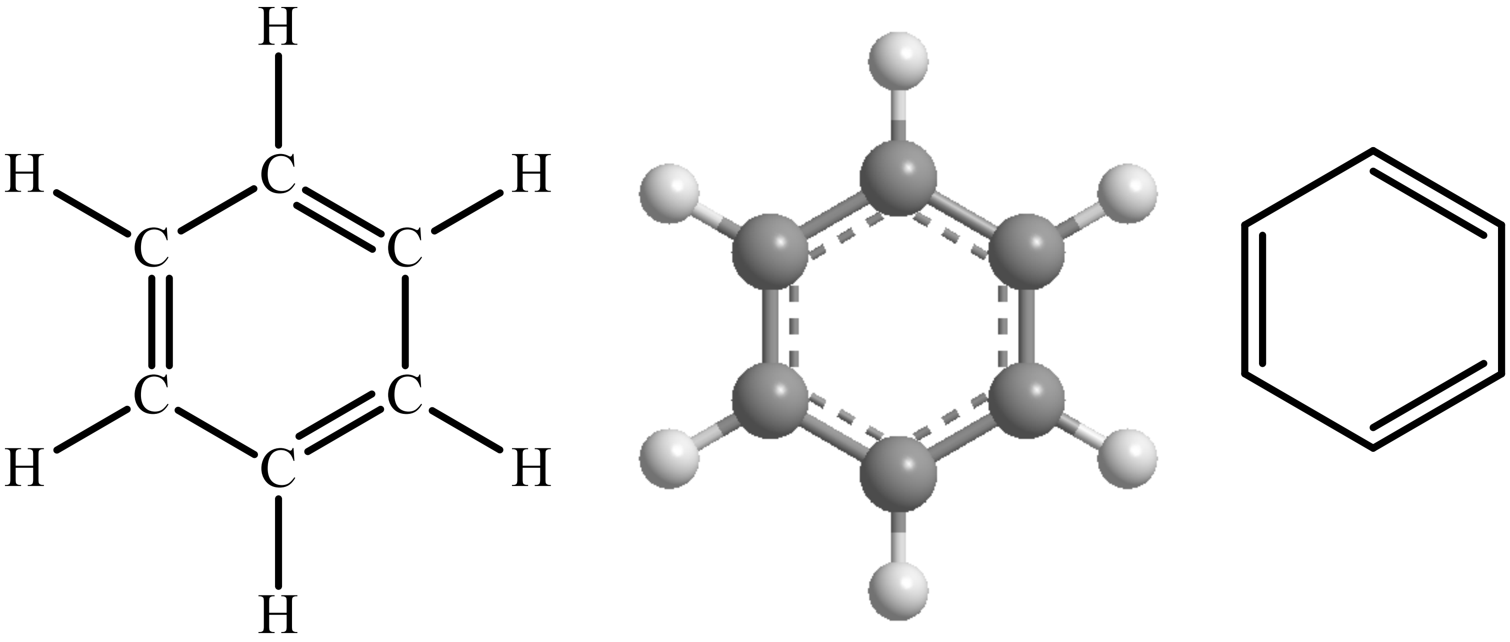
Aromatic hydrocarbons

Michael Faraday
(1791 –1867)

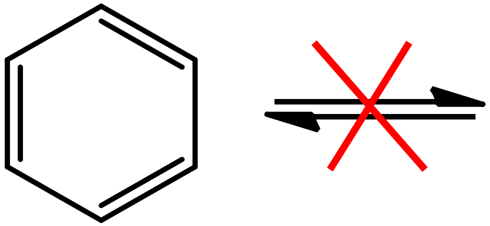
he chemistry of aromatic hydrocarbons is the chemistry of benzene

- it was isolated in 1825 by M. Faraday (himself) proving that the C: H ratio was 1: 1
- in 1834 E. Mitscherlich determines the brute formula: C_6H_6
- contrary to the strong reactivity of alkenes, benzene is not very reactive
- similar compounds with low C: H ratio had a pleasant odor e were, therefore, classified as aromatic (Kekulè, Couper, Boutlerov) in 1866 Kekulé proposed this structure

Friedrich A. Kekulé
von Stradonitz
(1829 –1896)



Kekulé immediately (wrongly) proposed the presence of isomers in benzene, and that there was a chemical balance between them

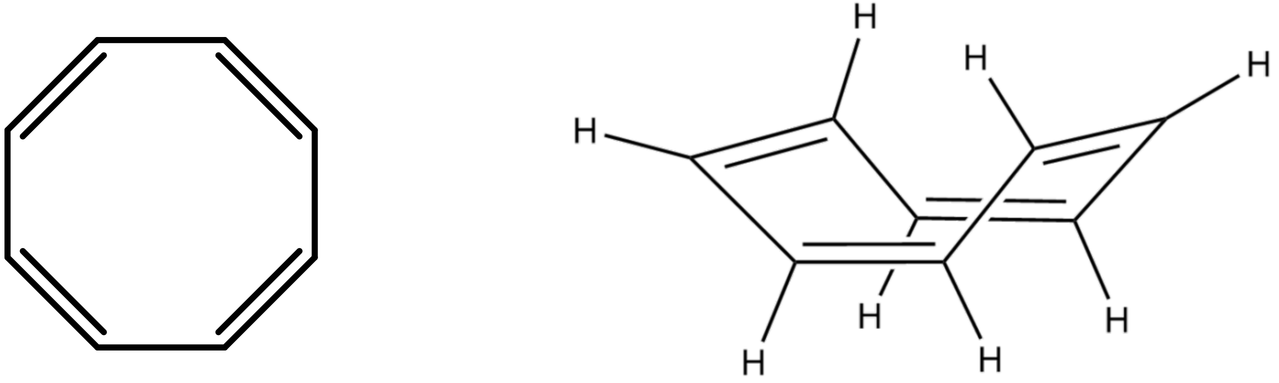


In reality these 2 structures are the same molecule, and are called resonance limit formulas (L. Pauling)

It was believed that the aromaticity was due to the presence of alternating double bonds

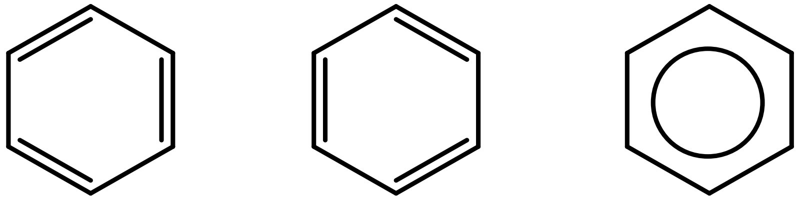
Cyclooctatetraene has 4 alternating double bonds and was proposed to be aromatic. However, and unlike benzene, it exhibits a certain chemical reactivity and was subsequently shown to have a non-planar structure, with longer single bonds (about 1.5Å) than double bonds (about 1.3Å).

8 π electrons

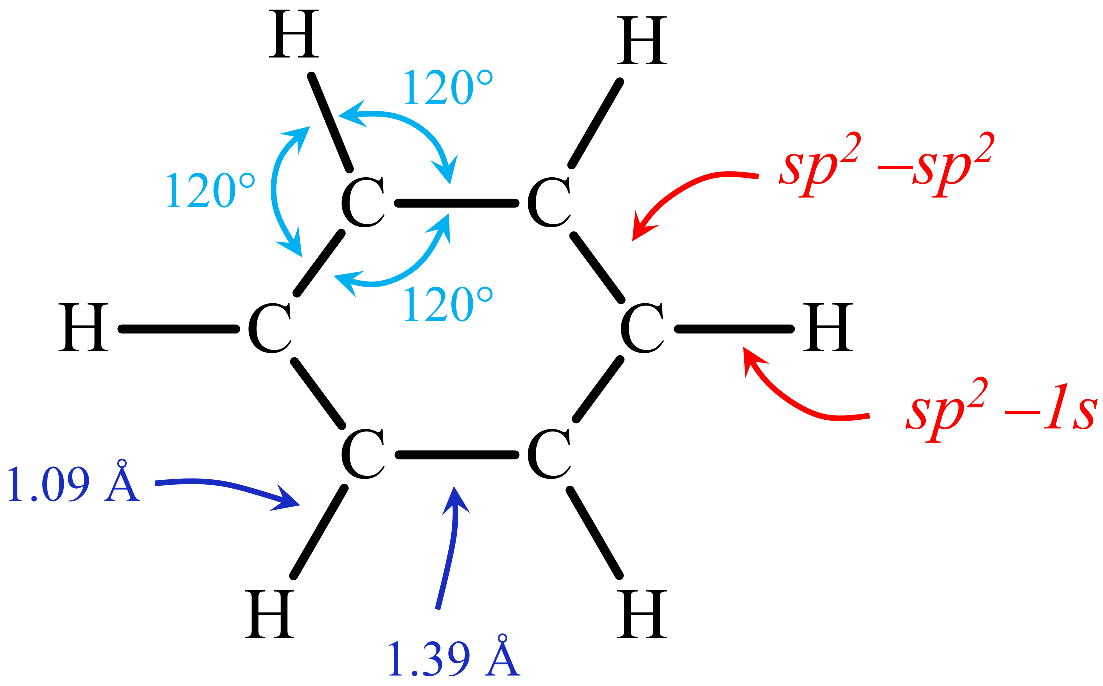


cyclooctatetraene

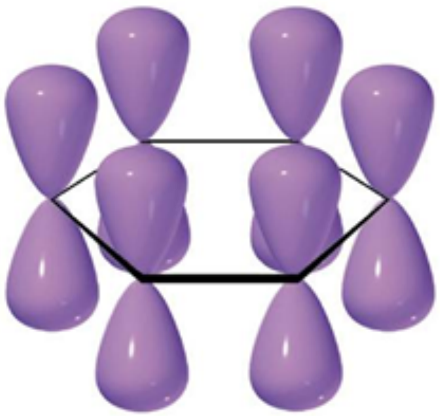
Benzene structure



The Kekulé structure implies the presence of alternating single and double bonds of different lengths. In benzene all C-C bonds are **equivalent** and have an intermediate **length** and **energy** between that of a simple bond and that of a double bond (~ 1.39 Å).



In benzene the 6 π electrons (aromatic sextet) of the non-hybridized 2p orbitals are found on a single molecular orbital located above and below the plane of the molecule.

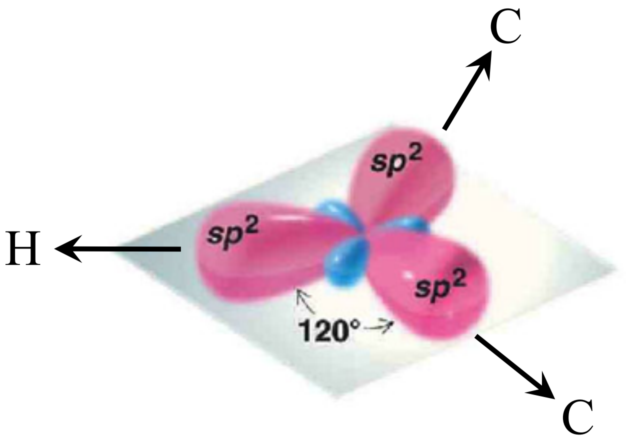


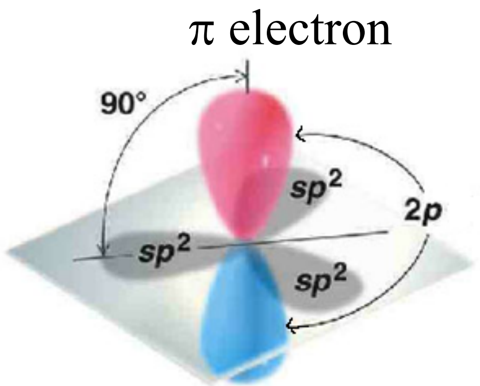
6 non hybridized 2p orbitale

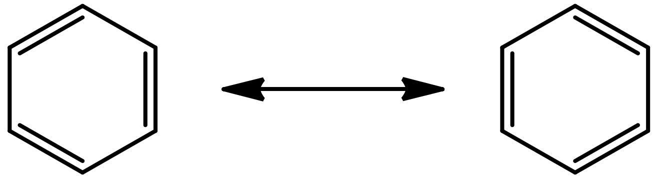
Molecular orbital

6 π electrons are delocalized throughout the benzene ring

To define the real structure of benzene we use the concept of resonance, considering benzene as a **resonance hybrid** between two limit formulas:

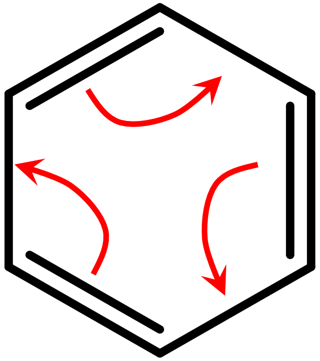






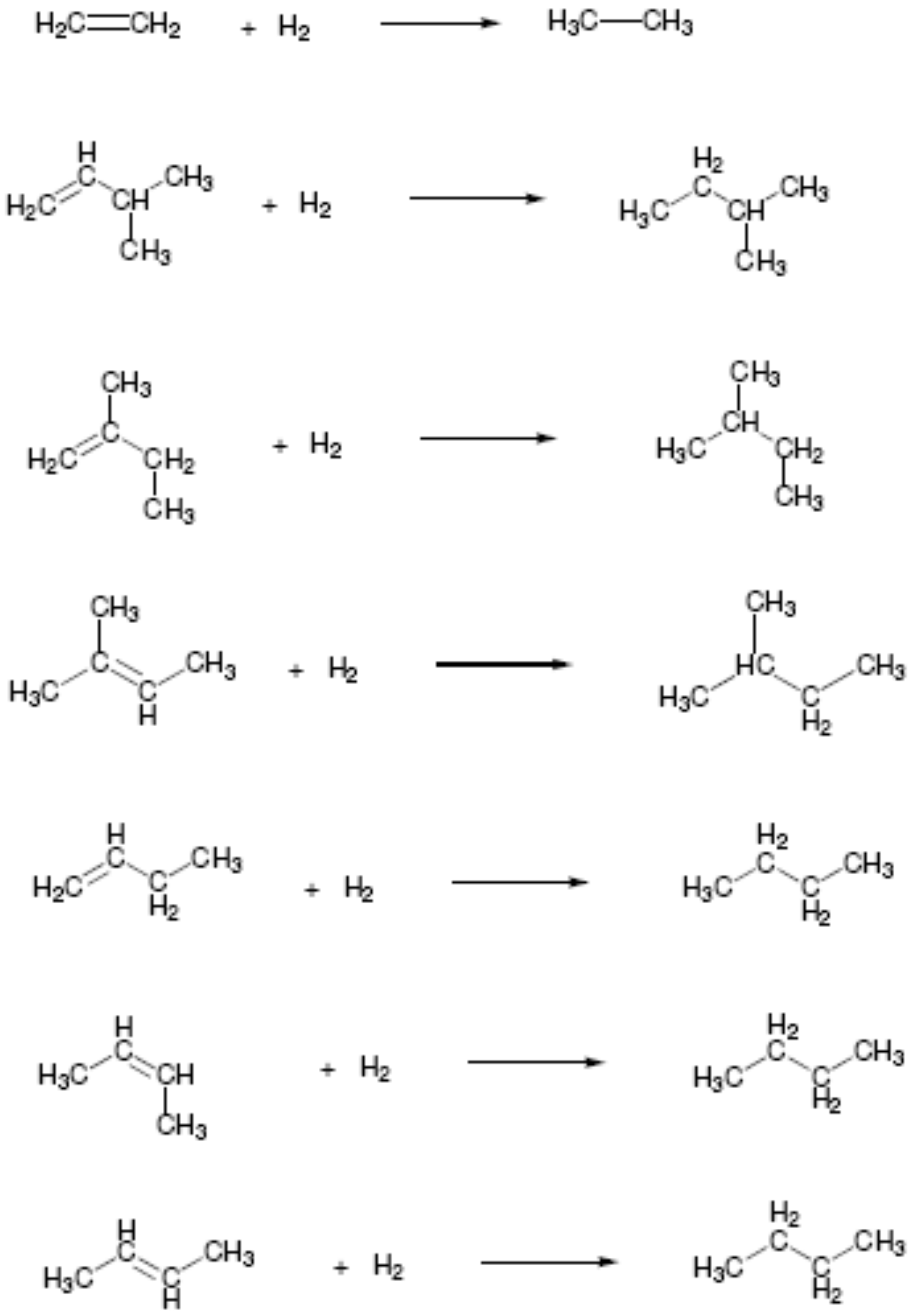
The arrow with 2 points indicates the resonance

How do you go from one resonance limit structure to another?



move pairs of π electrons from a double bond to a single bond by using curved arrows

How is the stability of benzene estimated? Heats of hydrogenation



ΔH° = –136.7 kJ/mol

ΔH° = –126.6 kJ/mol

ΔH° = –119 kJ/mol

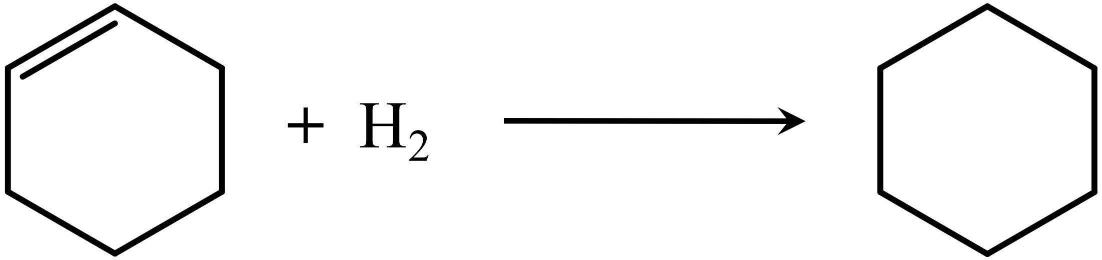
ΔH° = –112.4 kJ/mol

ΔH° = –127 kJ/mol

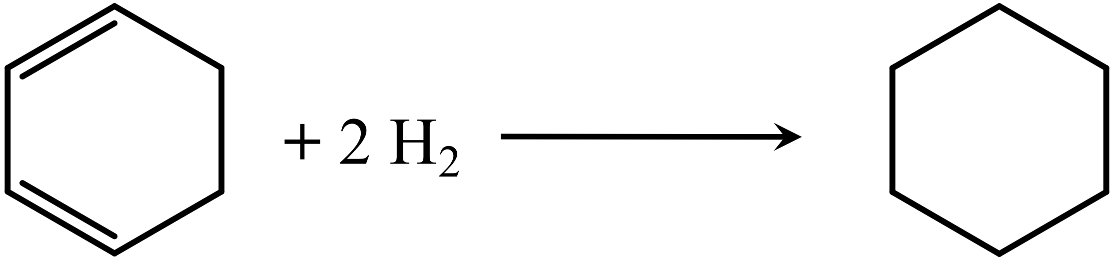
ΔH° = –120 kJ/mol

ΔH° = –115 kJ/mol

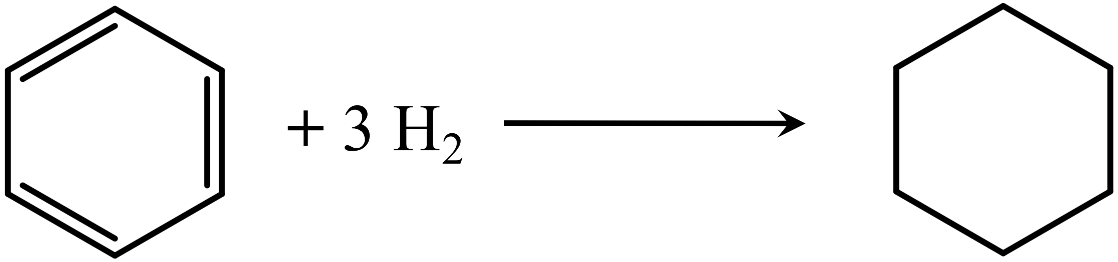
Come si stima la stabilità del benzene?



$\Delta H°_{osservato} = -120$ kJ/mol

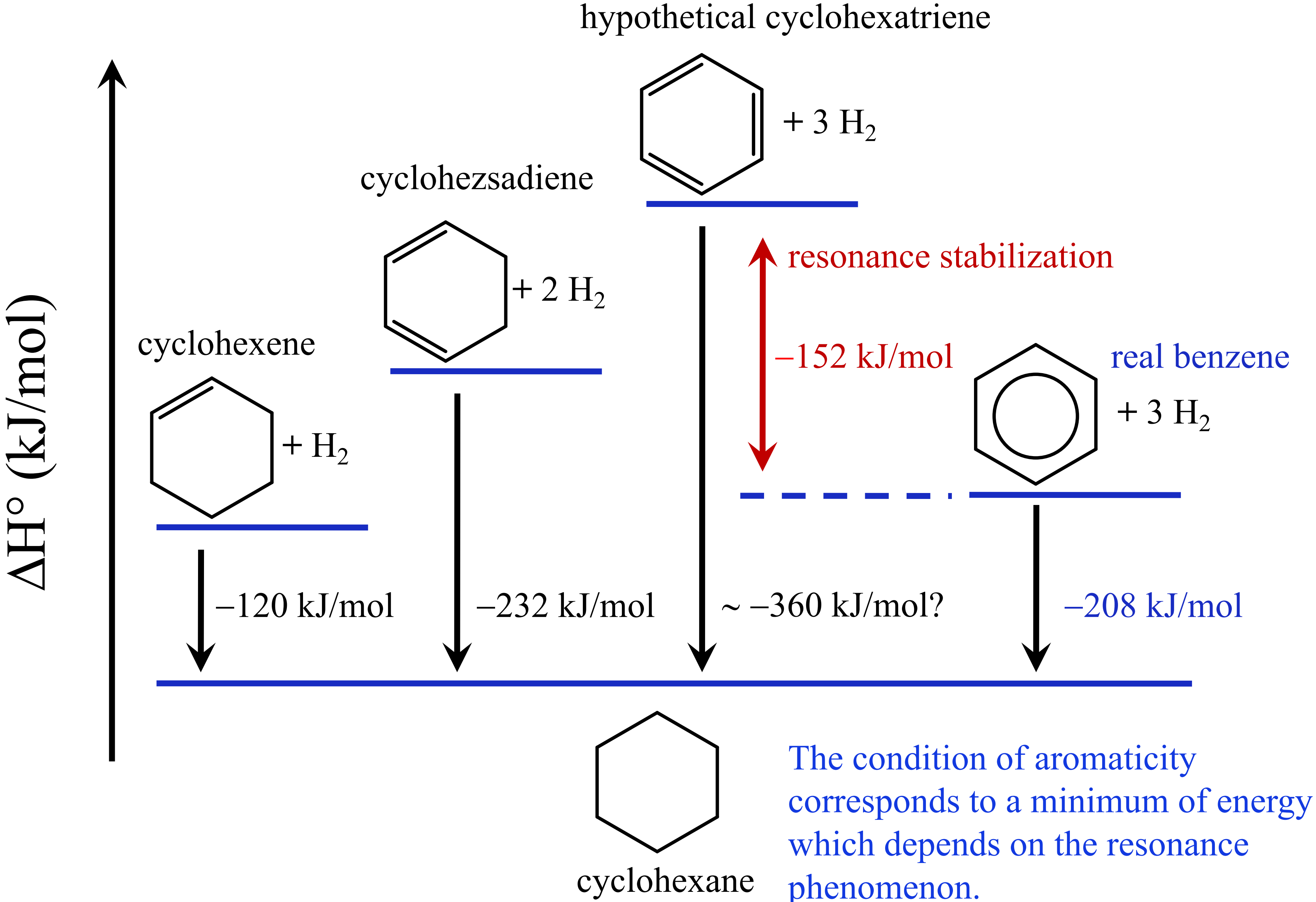


$\Delta H°_{aspettato} = -240$ kJ/mol
$\Delta H°_{osservato} = -232$ kJ/mol



$\Delta H°_{aspettato} = -360$ kJ/mol
$\Delta H°_{osservato} = -208$ kJ/mol

How is the stability of benzene estimated?



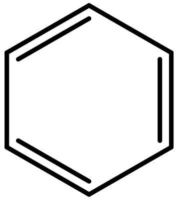
The condition of aromaticity corresponds to a minimum of energy which depends on the resonance phenomenon.

Hückel’s rule. Aromatic condition : (4n+2) π electrons

To be aromatic a compound with n rings must have cyclic electron clouds containing **4n + 2** delocalized π electrons (Hückel's rule, derived from quantum mechanical considerations). Therefore, delocalization is not a sufficient condition for aromaticity, but a certain number (6, 10, 14, etc.) of π electrons is also required.

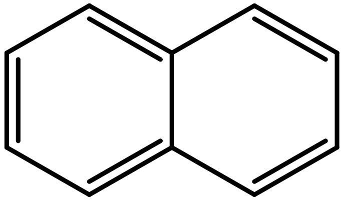
For example, a compound such as **cyclooctatetraene**, having 8 π electrons, cannot be aromatic and experimental data confirm this hypothesis (long and short C-C bonds).

benzene n=1



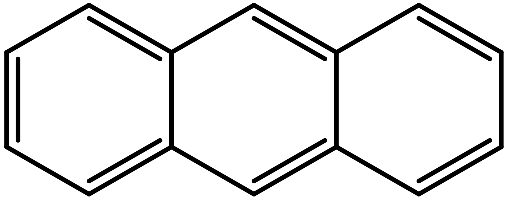
6

naphthalene n=2



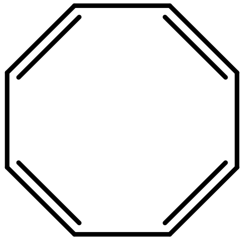
10

antracene n=3



14

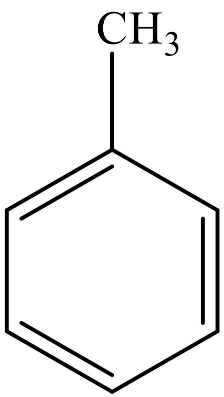
cyclooctatetraene n=1



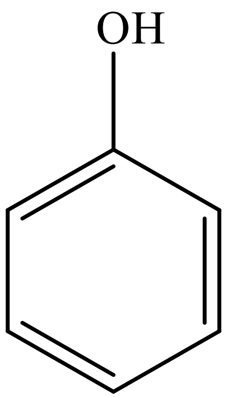
8

π electrons

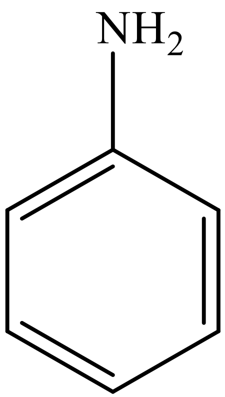
Some derivatives of benzene



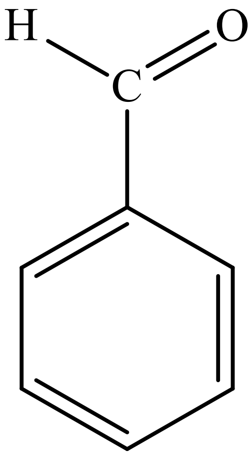
toluene



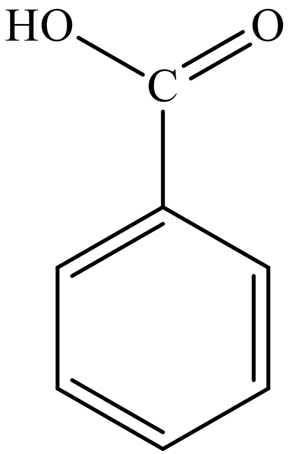
fenol



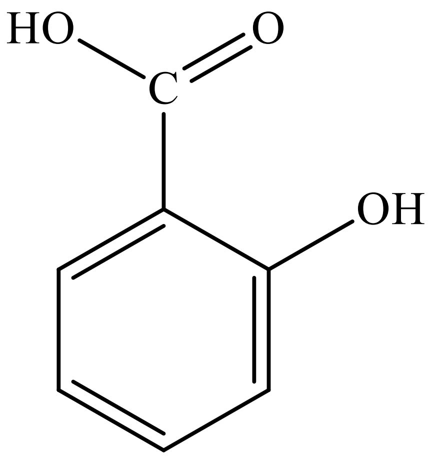
aniline



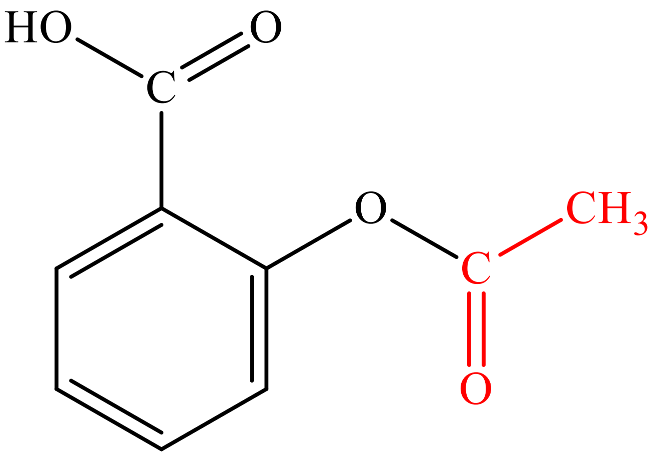
benzaldehyde



benzoic acid



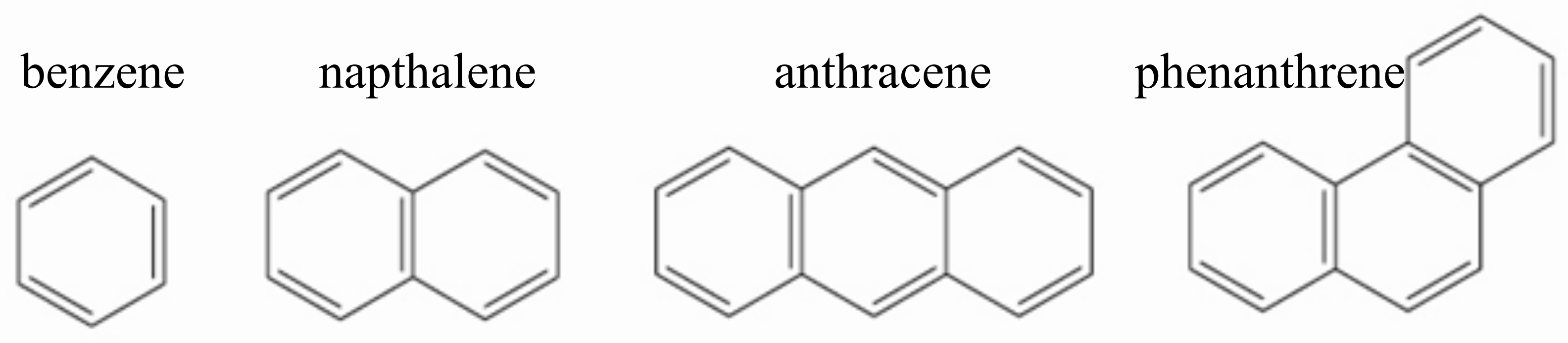
salicylic acid



acetylsalicylic acid

aspirine

Condensed ring derivatives of benzene.

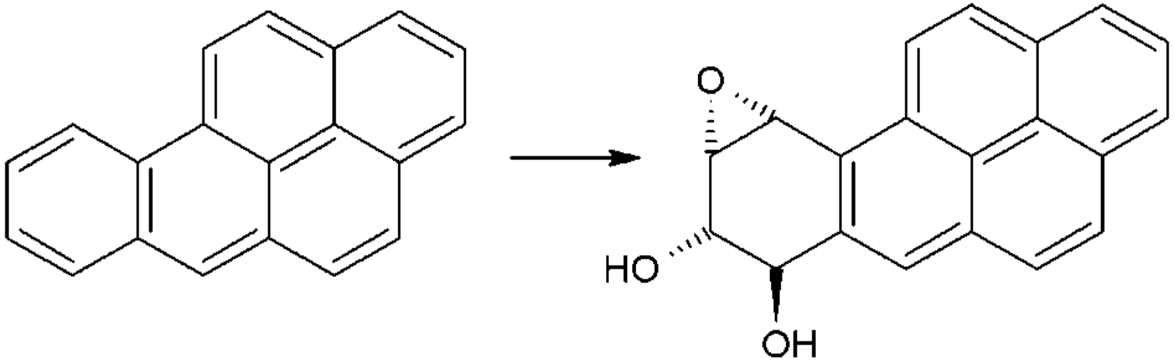


resonance (kJ/mol)	152	255	347	381

They all have a planar structure and have electronic delocalization over the entire molecule. They are produced by the combustion of fuel oils, coal, tobacco and organic materials. They are DNA intercalating agents and can have mutagenic effects.

Carcinogenicity of benzopyrene

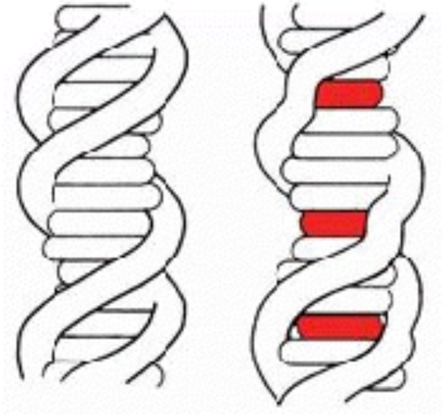
enzymatic oxidation of benzopyrene

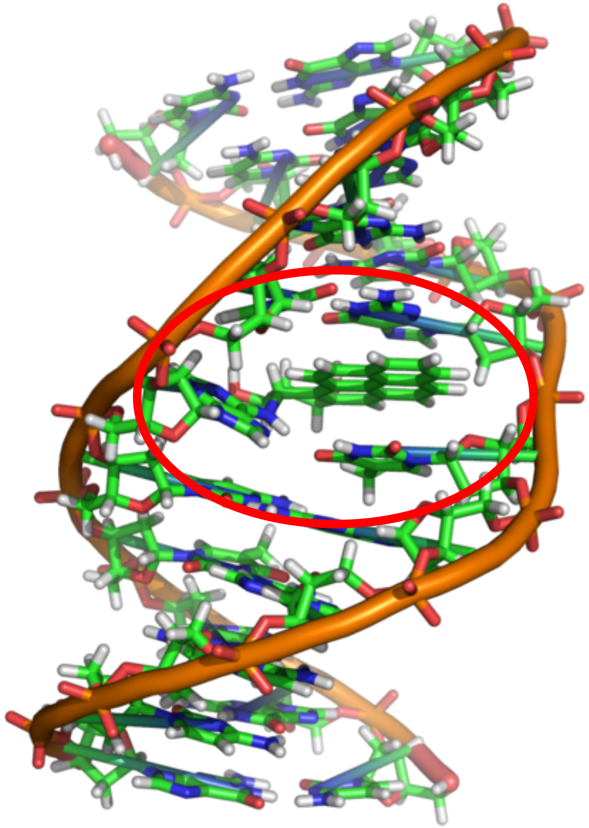


Benzopyrene
(procarcinogen)

benzopyrene diol epoxide
(intercalating species)

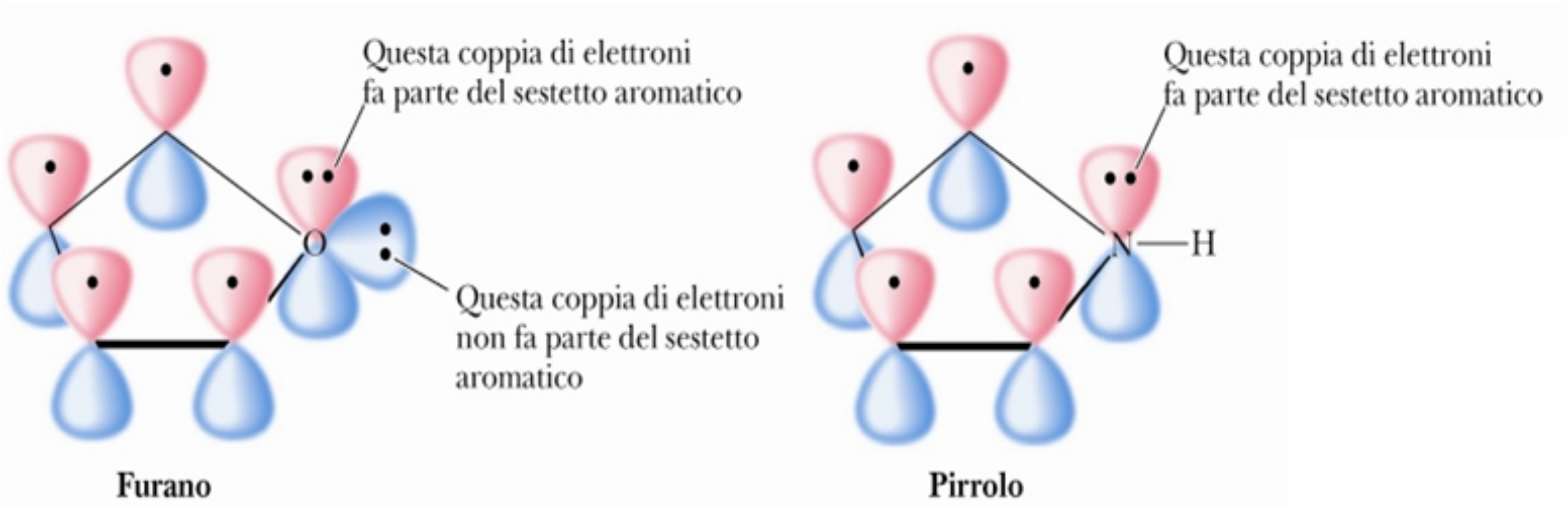
This molecule is a DNA intercalator that disrupts the structure of the double helix. It covalently binds to guanine nucleotides. The DNA duplication process is therefore compromised by also increasing the frequency of mutations, which lead to cancer.





Heterocyclic aromatic compounds

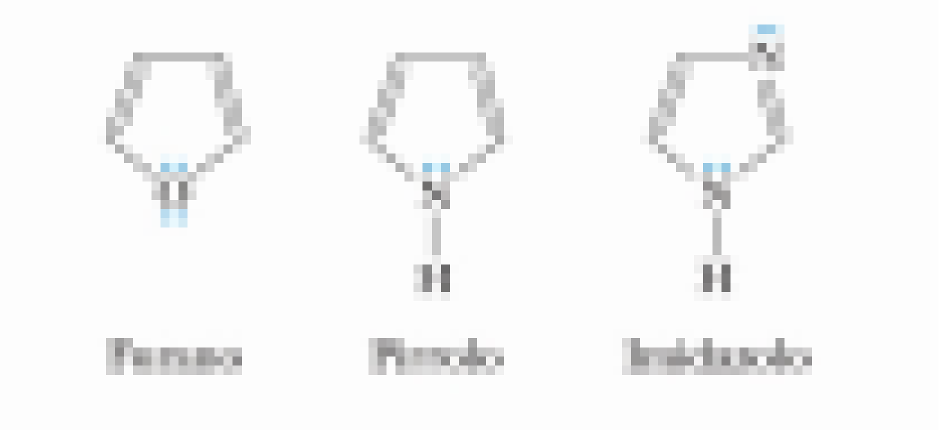
Cyclic molecules in which Huckel's rule is respected, and in which in the ring there are one or more atoms other than carbon (**heteroatoms**).



Questa coppia di elettroni fa parte del sestetto aromatico

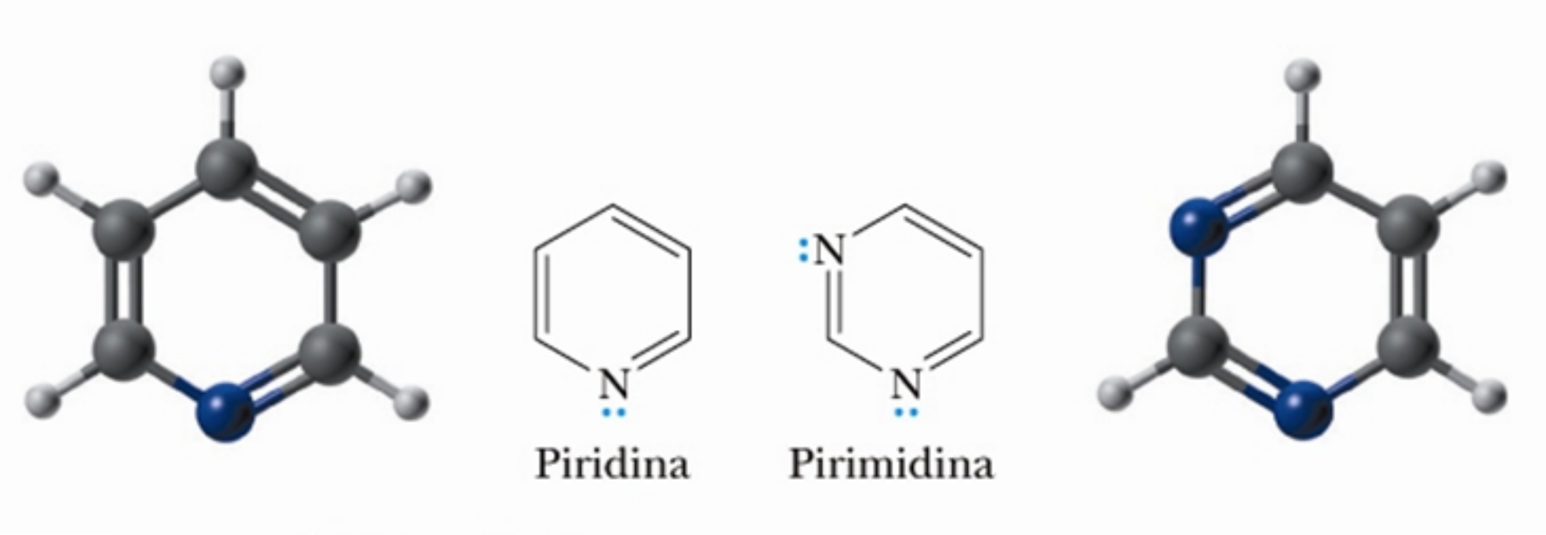
Questa coppia di elettroni non fa parte del sestetto aromatico

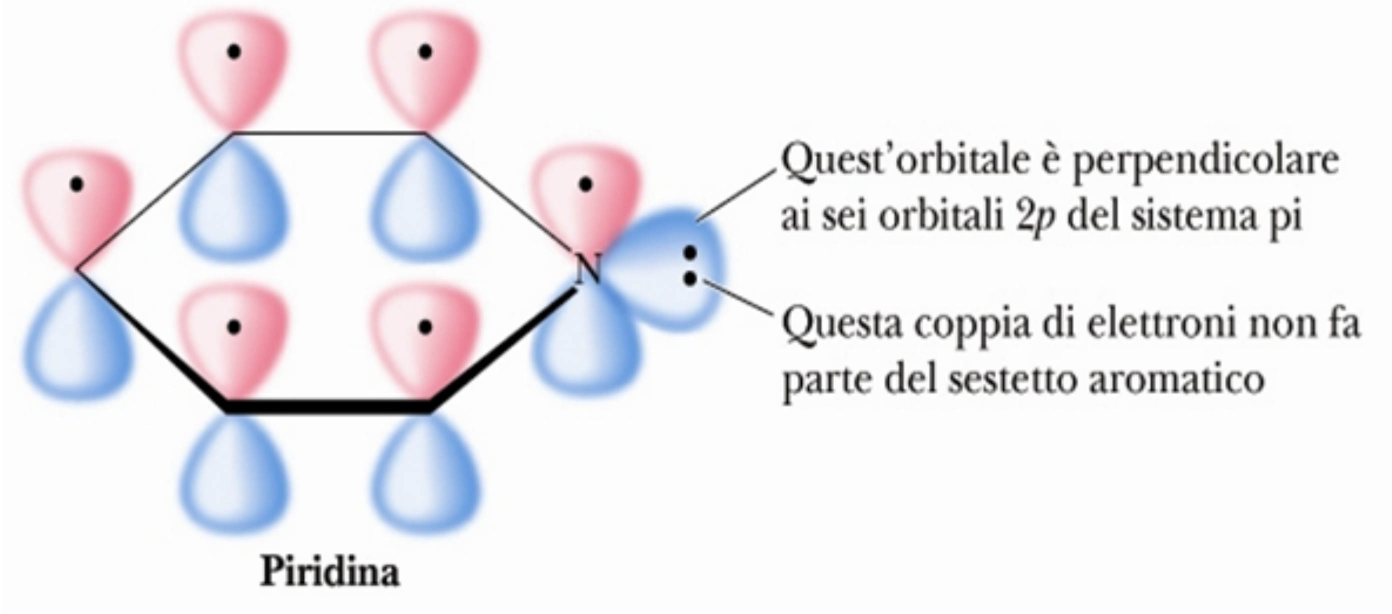
Questa coppia di elettroni fa parte del sestetto aromatico



Se una coppia solitaria non fa parte del sestetto aromatico il composto ha proprietà basiche.

Derivati della pirimidina sono tra le basi azotate aromatiche che costituiscono gli acidi nucleici.



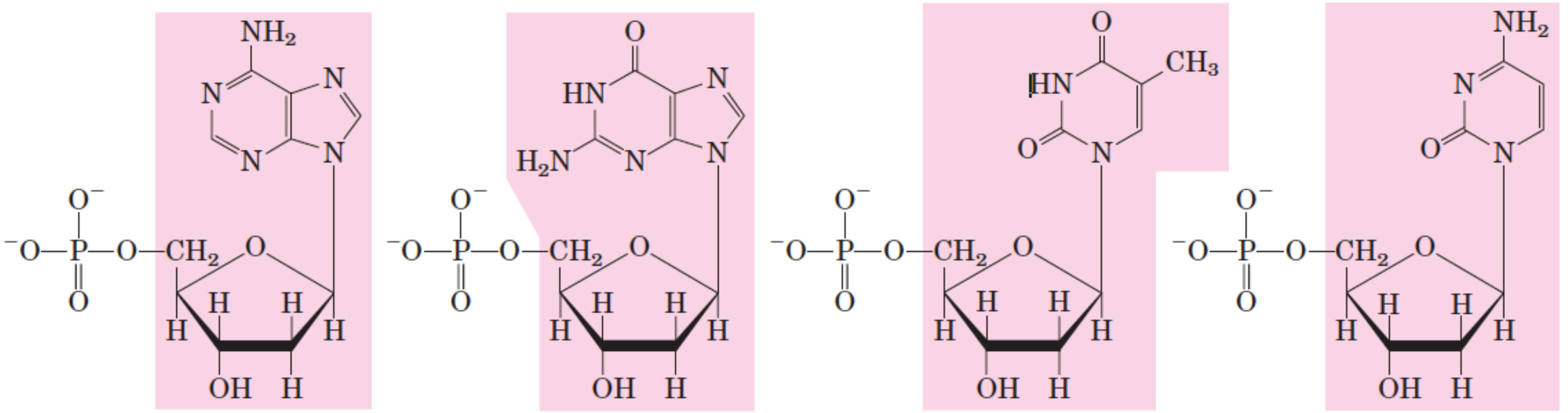


Quest'orbitale è perpendicolare ai sei orbitali 2*p* del sistema pi

Questa coppia di elettroni non fa parte del sestetto aromatico

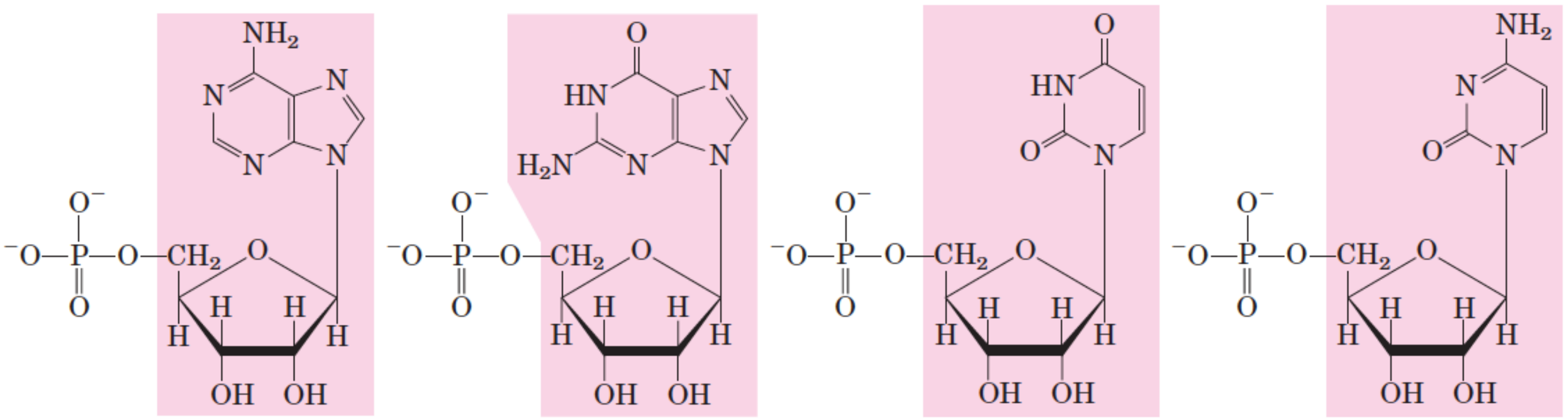
Piridina

The aromatic nitrogenous bases and nucleic acids.



Nucleotide:	Deoxyadenylate (deoxyadenosine 5′-monophosphate)	Deoxyguanylate (deoxyguanosine 5′-monophosphate)	Deoxythymidylate (deoxythymidine 5′-monophosphate)	Deoxycytidylate (deoxycytidine 5′-monophosphate)
Symbols:	A, dA, dAMP	G, dG, dGMP	T, dT, dTMP	C, dC, dCMP
Nucleoside:	Deoxyadenosine	Deoxyguanosine	Deoxythymidine	Deoxycytidine

(a) Deoxyribonucleotides



Nucleotide:	Adenylate (adenosine 5′-monophosphate)	Guanylate (guanosine 5′-monophosphate)	Uridylate (uridine 5′-monophosphate)	Cytidylate (cytidine 5′-monophosphate)
Symbols:	A, AMP	G, GMP	U, UMP	C, CMP
Nucleoside:	Adenosine	Guanosine	Uridine	Cytidine

(b) Ribonucleotides

Le basi azotate aromatiche che degli acidi nucleici.

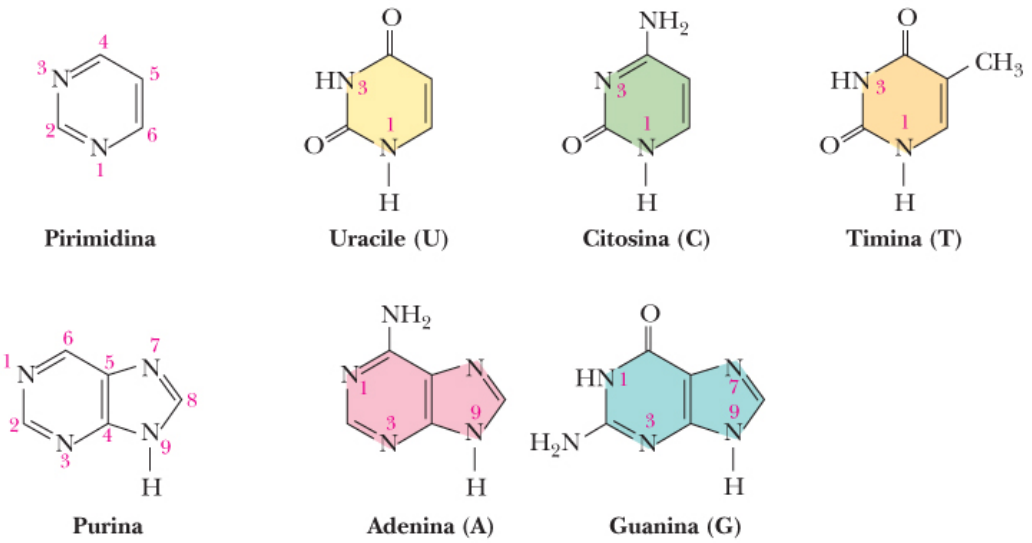


Figura 20.1
Nomi e abbreviazioni a una lettera usate per le basi azotate eterocicliche aromatiche più comuni presenti nel DNA e nell'RNA. Gli atomi dei cicli che costituiscono le basi sono numerati secondo gli stessi criteri usati per i composti capistipite, la pirimidina e la purina.

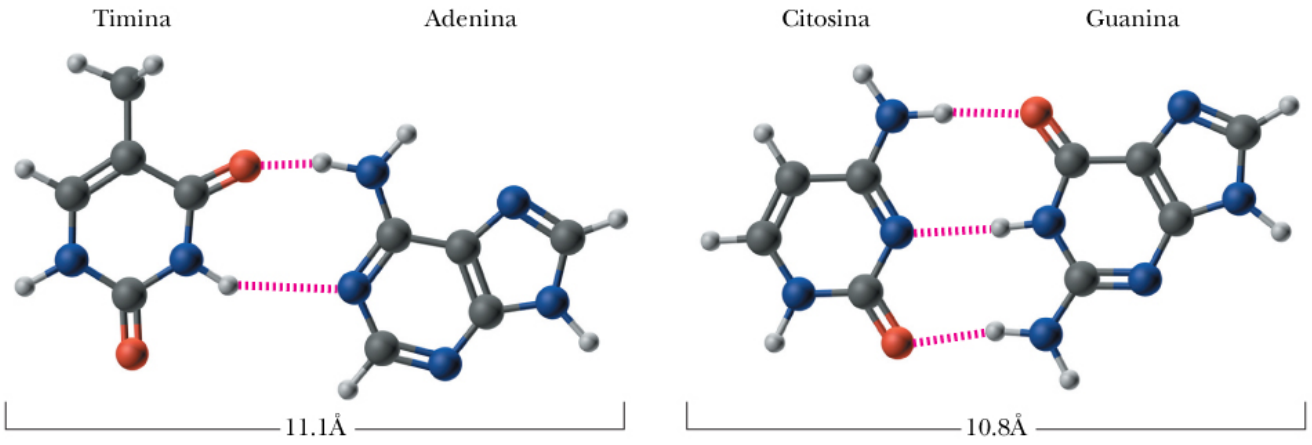


Figura 20.7
L'accoppiamento di basi tra adenina e timina (A-T) e tra guanina e citosina (G-C). La coppia di basi A-T è tenuta insieme da due legami idrogeno, mentre la coppia G-C da tre.

L'accoppiamento specifico fra le basi azotate e la complementarietà di forma tra purine e pirimidine permettono al DNA di replicarsi.

Modificata da Brown & Poon
Introduzione alla chimica organica