

# ORGANIC STEREOCHEMISTRY - I

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## Basic books

- Organic stereochemistry, Henri Kagan (1979)
- Stereochemistry of organic compounds**, Ernest L. Eliel (1994)
- Stereochemia w syntezie organicznej, Jacek Gawroński (1988)
- Stereochemia: podstawy i zastosowania, Mihály Nógrádi (1988)
- Classics in Stereoselective Synthesis, E.M. Carreira, L. Kvaerno (Wiley, 2009)

## *Mile-Stones (historically) in stereochemistry*

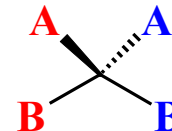
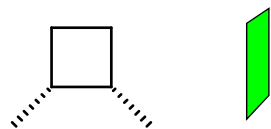
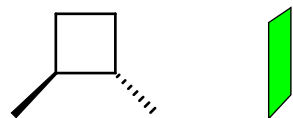
1. Pasteur 1860; van't Hoff 1874; Le Bel 1874
2. Conformational analysis: Hughes and Ingold (1935, 1953), **Barton** (1950)
3. Cahn, Ingold, **Prelog** rule: 1966
4. Stereochemistry and topology: **Prelog** 1969
5. Reactivity and stereochemistry (**NOBEL**: Fischer 1902; Haworth, Karrer 1937; Robinson 1947; Todd 1957; Pauling 1954; Woodward 1965; Barton, Hassel 1969; Cornforth, Prelog 1975; Fukui, Hoffmann 1981; Sharpless, Noyori, Knowles 2001)

**Isomers** – compounds with identical molecular formula differing in the structure

**Structural isomers (stereoisomers) C<sub>5</sub>H<sub>8</sub>**

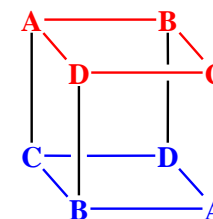
**Steric isomers (stereoisomers) C<sub>5</sub>H<sub>8</sub>**

## Are the object and its mirror image identical??

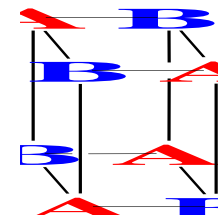


### Elements of symmetry

1. Axis of symmetry (normal)  $C_n$
2. Plane of symmetry  $\sigma$
3. Center of symmetry  $i$



### Higher order alternate axes

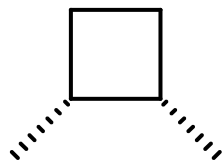
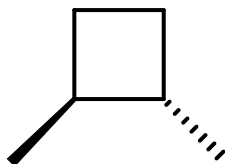


# Find the elements of symmetry in the molecule

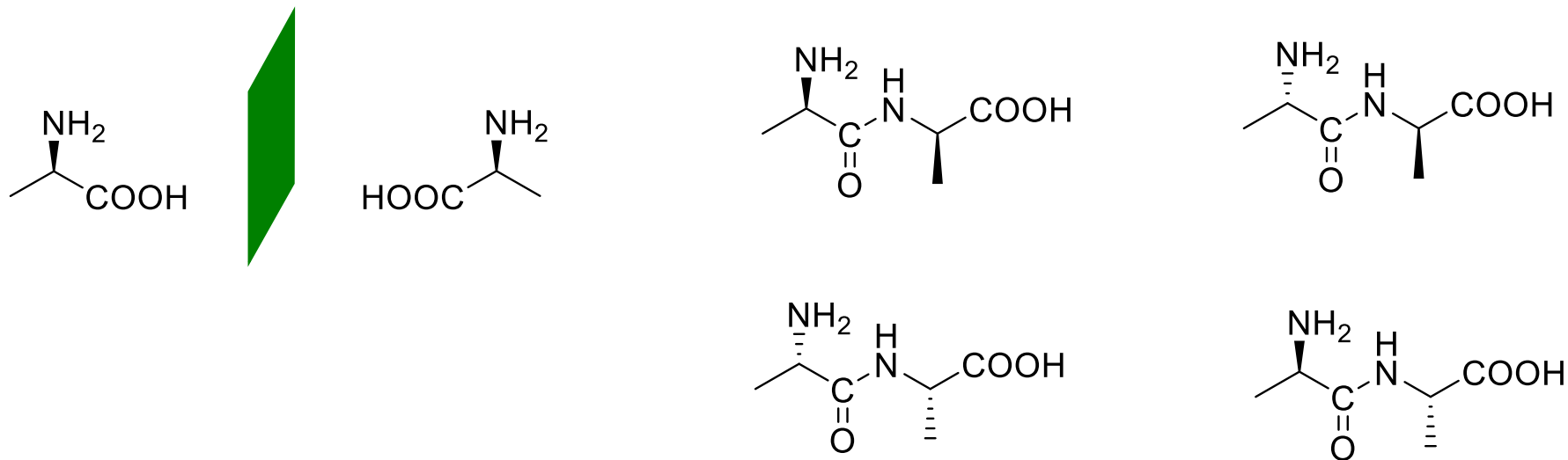
axis

plane

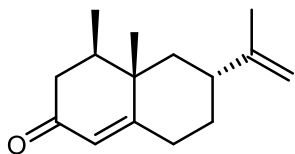
center



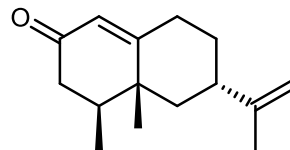
# Enantiomers - diastereoisomers



# Enantiomers CAN be seen differently by the living organisms

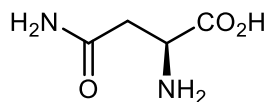


grapefruit odor

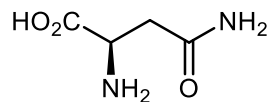


woody odor

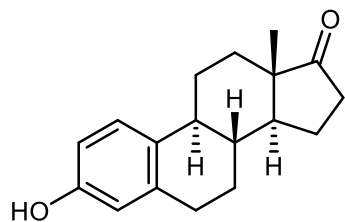
The Nose as a Stereochemist. Enantiomers and Odor, R. Bentley, *Chem. Rev.* **2006**, *106*, 4099-4112



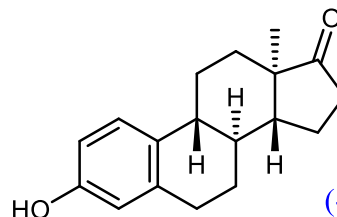
L-asparagine  
bitter taste



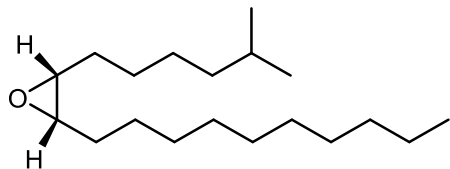
D-asparagine  
sweet taste



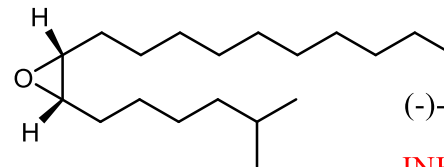
(+) - estrone  
active hormone



(-) - estrone  
not active



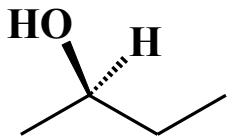
(+)-disparlure  
active pheromone



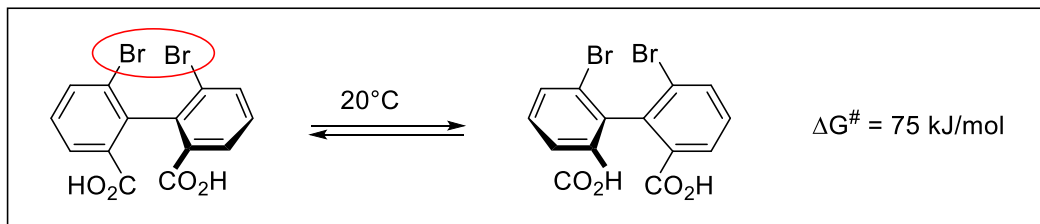
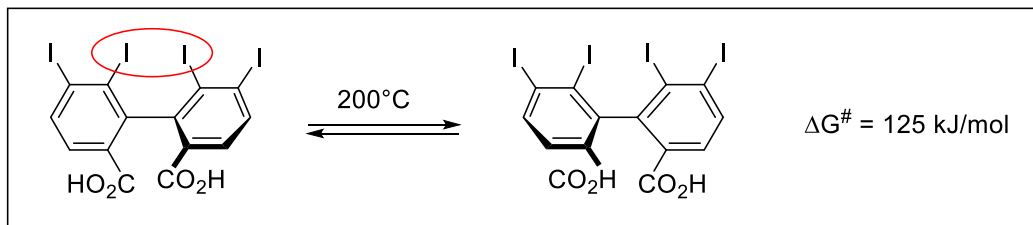
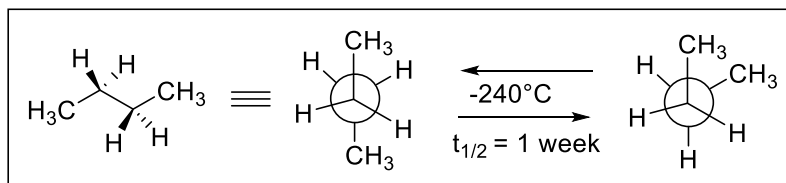
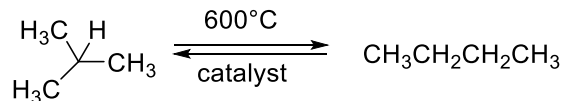
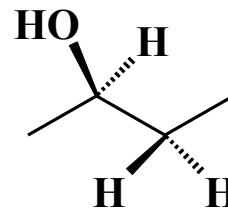
(-)-disparlure

**INHIBITOR !!!!**

**CONFIGURATION** Steric  
(**PERMANENT**) arrangement  
of atoms (groups) in the molecule

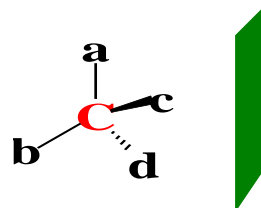


**CONFORMATION LABILE**, arrangement of atoms  
(groups) in the molecule. Individual conformers are  
**easily** interconverted

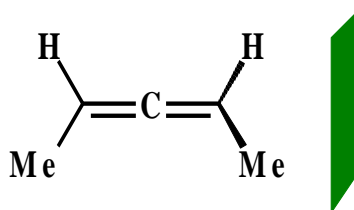


# MOLECULAR CHIRALITY

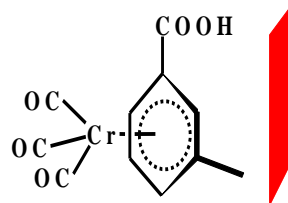
*Stereogenic Center*  
point



*Axial chirality*



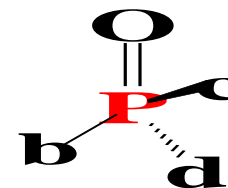
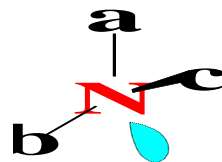
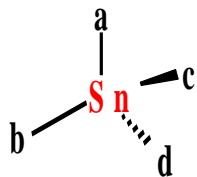
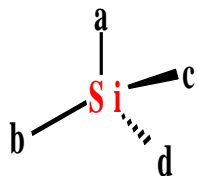
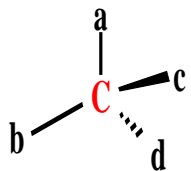
*Planar chirality*  
(plane of symmetry)



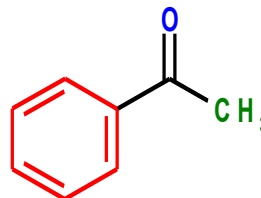
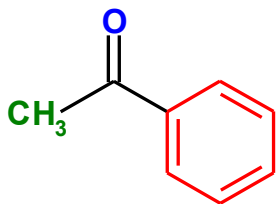
Binaphthol and derivatives: *Chem. Rev.* **2005**, *105*, 857–89. *Chem. Rev.* **2013**, *113*, 6234–6458

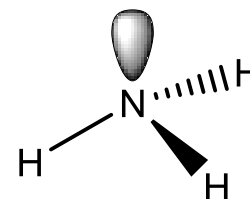
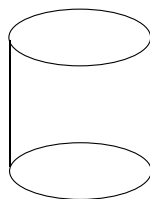
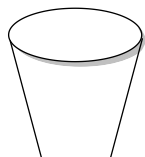
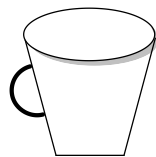


## STEREOGENIC CENTER



The *re* and *si* sides of the molecule





### Schoenflies' point groups of symmetry

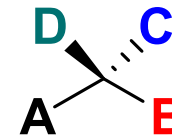
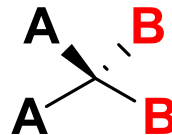
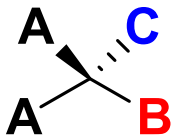
Chiral groups	Achiral Groupus
$C_n$ (only one $C_n$ axis)	$C_s$ (only one $\sigma$ )
$D_n$ ( $C_n + n \perp C_2$ )	$S_n$ ( <u>no</u> $\sigma$ n even)
$T$ ( $4C_3 + 3C_2$ , <u>no</u> $\sigma$ )	$C_{nv}$ ( $C_n + n \sigma_v$ <u>no</u> $\sigma_h$ )
	$C_{nh}$ ( $C_n + \sigma_h$ <u>no</u> $\sigma_v$ )
	$D_{nd}$ ( $C_n + n \perp C_2 + n \sigma_v$ <u>no</u> $\sigma_h$ )
	$D_{nh}$ ( $C_n + n \perp C_2 + n \sigma_v + \sigma_h$ )
	$T_d$ ( $4C_3 + 3C_2$ , 6 $\sigma$ )

## Classification of the groups according to their symmetry. Schoenflies' point groups

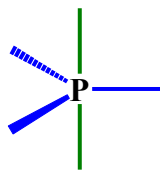
Objects (molecules) can be classified according to their symmetry.

Classification is much easier when we consider the presence (or not) the ALTERNATE axis ( $S_n$ ). The operation generated by this axis requires the rotation  $360/n$  + flip in horizontal plane ( $\sigma_h$ ). This means that the row of this axis must be even

From the point of view of symmetry the molecules (objects) are either **chiral** (no axis  $S_n$ ) or **achiral** (presence of  $S_n$ )



Stereoisomerism of  
5-coordinated compounds



find elements of symmetry in  $Paabcd$

