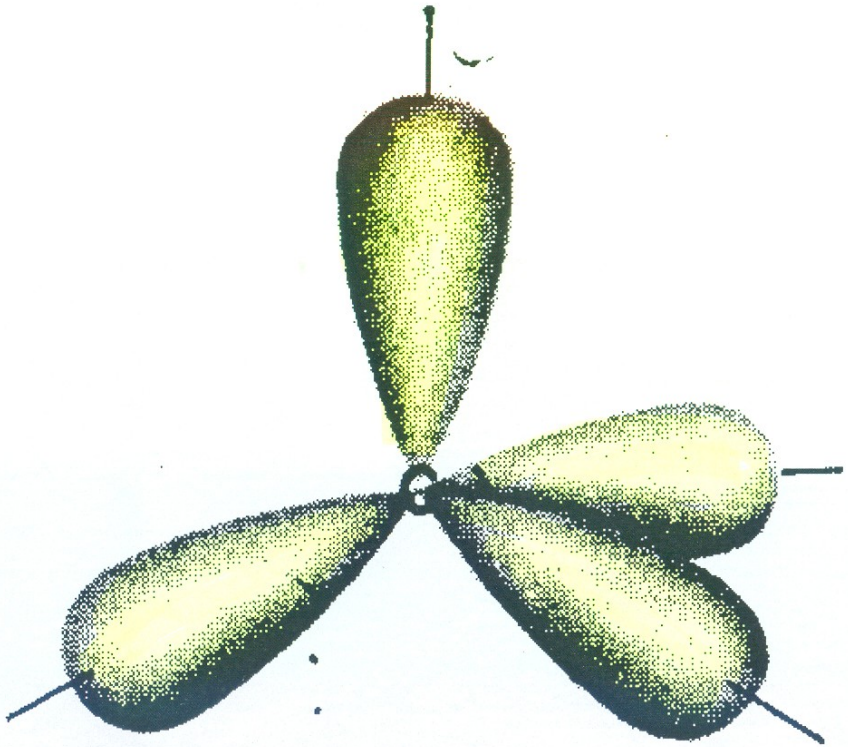
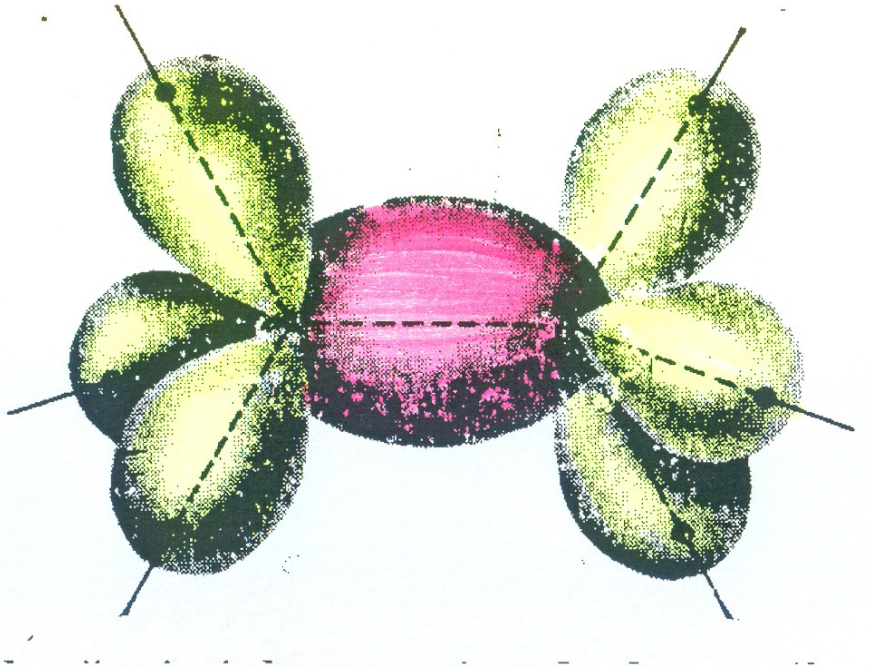
SATURATED HYDROCARBONS – ALKANES AND CYCLOALKANES





BONDS

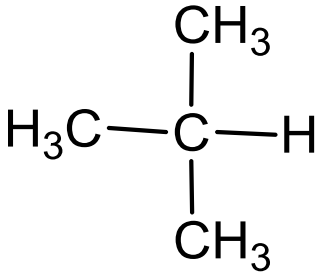
C – C	**0,154 nm**	**345 kJ/mol**	**only small difference in electronegativity**
C - H	**0,109 nm**	**427 kJ/mol**	**energy of this bond depends upon the position C atom in the structure**

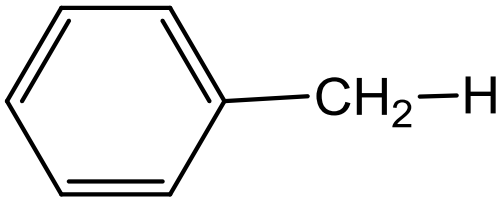
chain isomers

SATURATED HYDROCARBONS – ALKANES AND CYCLOALKANES

Tabulka 1.2. Dependence of bond energy upon the structure

CH_3-H	427	$(CH_3)_2CH-H$	393	C_6H_5-H	427
C_2H_5-H	405			$C_6H_5-CH_2-H$	326
$n-C_3H_7-H$	405	$(CH_3)_3C-H$	381	$CH_2=CH-H$	435



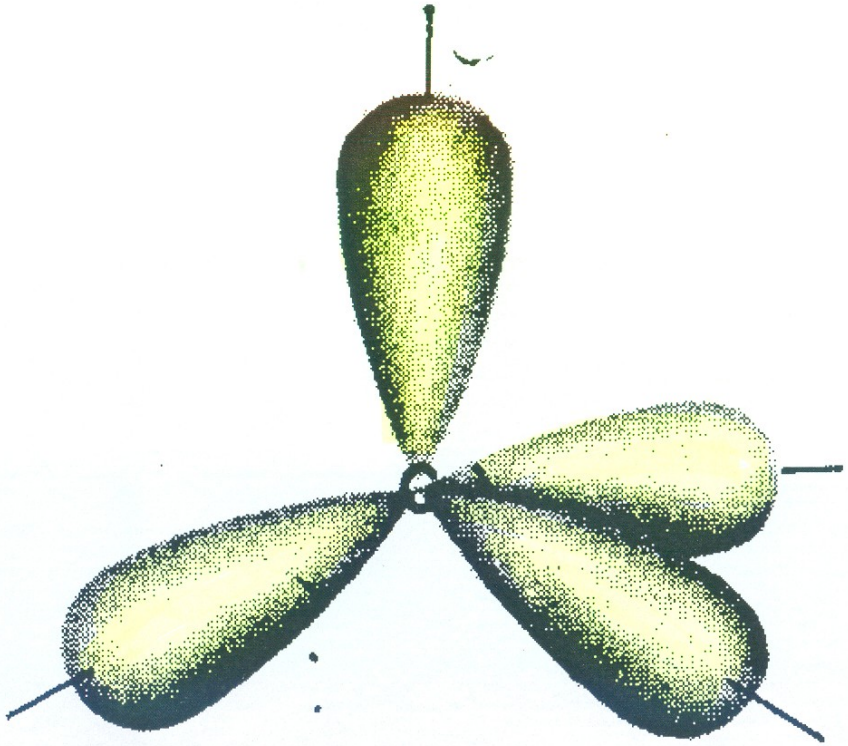


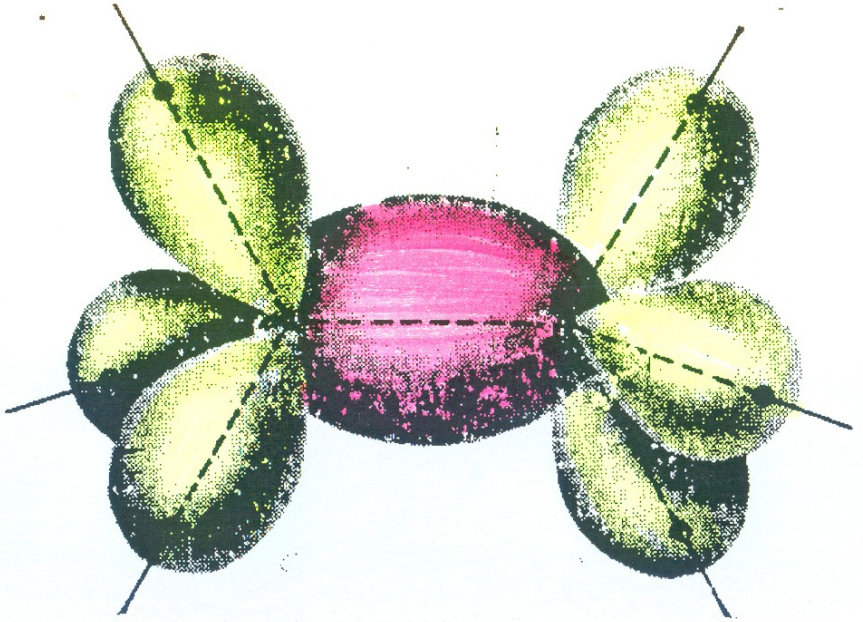
CHAIN ISOMERISM

Physical Constants of the Butane, Pentane, and Hexane Isomers

MOLECULAR FORMULA	STRUCTURAL FORMULA	mp °C	bp °C	DENSITY	INDEX OF REFRACTION n_D 20°C
C_4H_{10}	$CH_3CH_2CH_2CH_3$	−138.3	−0.5	0.6012_4^0	1.3543
C_4H_{10}	$CH_3CH(CH_3)CH_3$	−159	−12	0.603_4^0	—
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	−129.72	36	0.6262_4^{20}	1.3579
C_5H_{12}	$CH_3CH(CH_3)CH_2CH_3$	−160	27.9	0.6197_4^{20}	1.3537
C_5H_{12}	$CH_3C(CH_3)_2CH_3$	−20	9.45	0.61350_4^{20}	1.3476
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	−95	68	0.65937_4^{20}	1.3748
C_6H_{14}	$CH_3CH(CH_3)CH_2CH_2CH_3$	−153.67	60.3	0.6532_4^{20}	1.3714
C_6H_{14}	$CH_3CH_2CH(CH_3)CH_2CH_3$	−118	63.265	0.6643_4^{20}	1.3765
C_6H_{14}	$CH_3CH(CH_3)CH(CH_3)CH_3$	−128.8	58	0.6616_4^{20}	1.3750
C_6H_{14}	$CH_3C(CH_3)_2CH_2CH_3$	−98	49.7	0.6492_4^{20}	1.3688

CONFORMATIONAL ANALYSIS





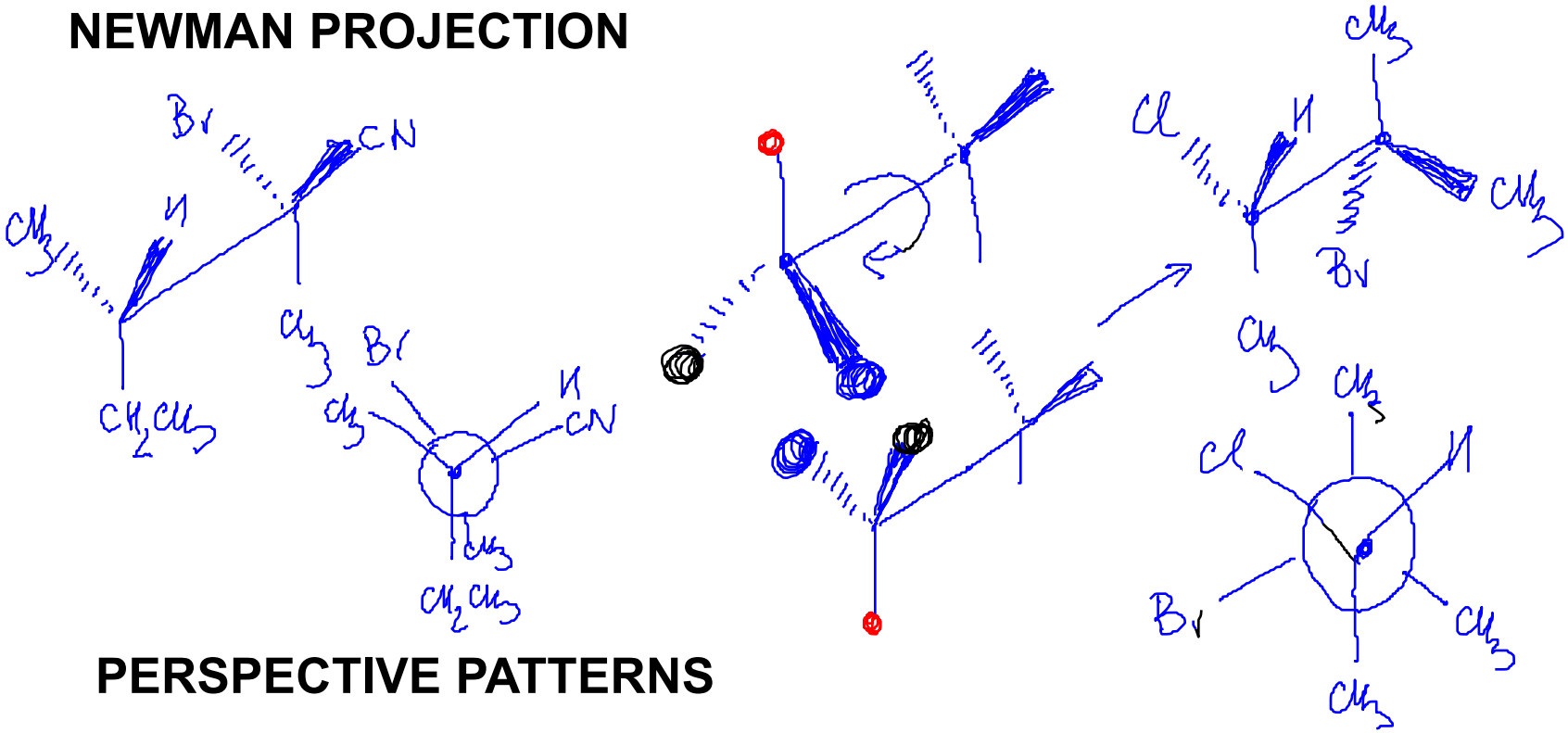
CONFORMATIONAL ISOMERISM - CONFORMERS

NEWMAN PROJECTION

ethan_energ.wrl

CONFORMATIONAL ANALYSIS

NEWMAN PROJECTION



PERSPECTIVE PATTERNS

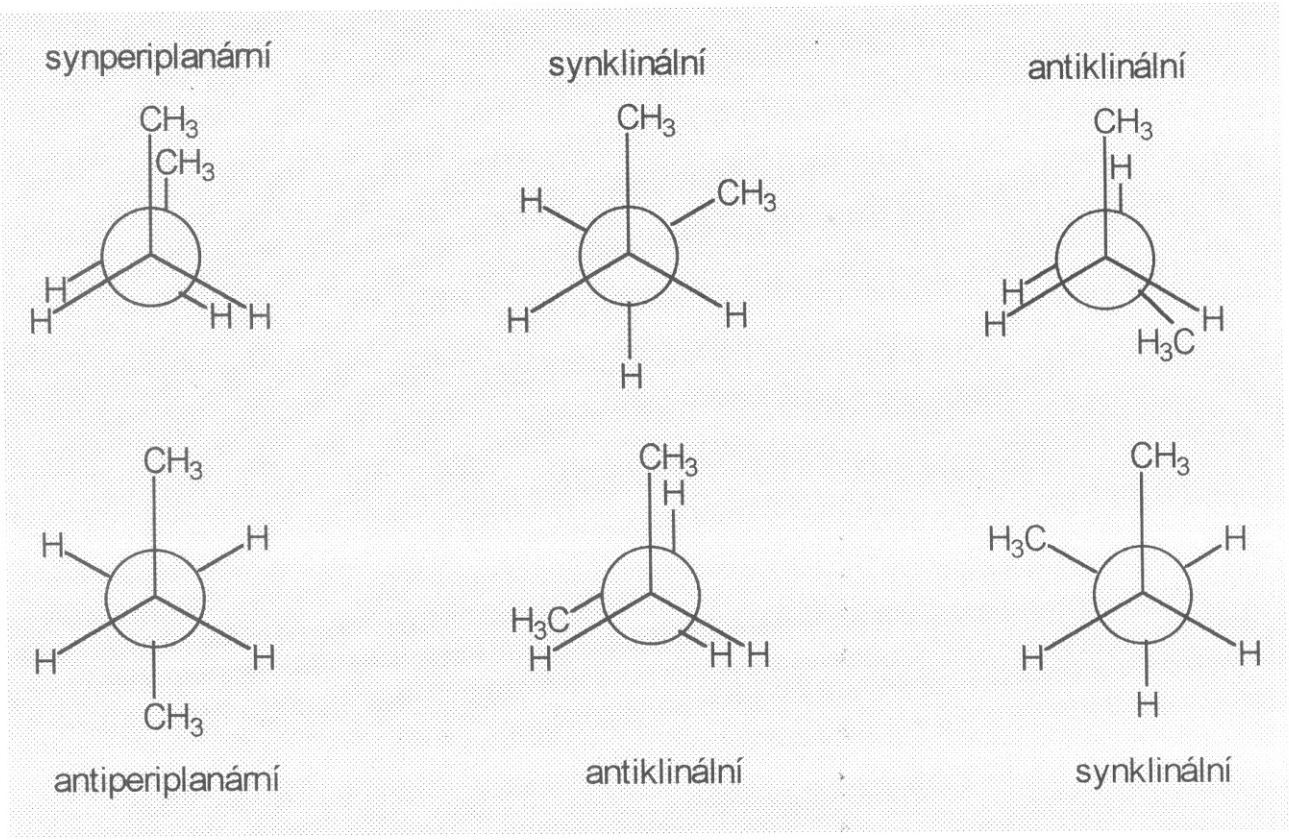
CONFORMATIONS OF BUTANE

butan_energ.wrl

CONFORMATIONAL ANALYSIS

NEWMAN PROJECTION

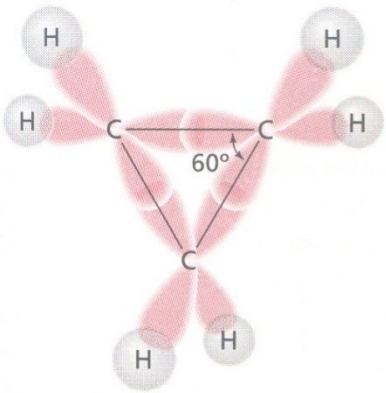
synperiplanar | synclinal | anticlinal



Antiperiplanar | anticlinal | synclinal

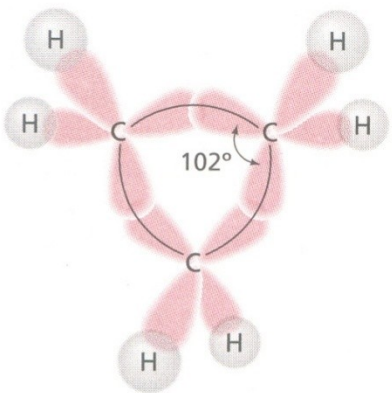
CYCLOALKANES AND THEIR STRUCTURE

Number of atoms in ring	Energy released when compounds burned related to CH_2 kJ/mol	Number of atoms in ring	Energy released when compound burned related to CH_2 kJ/mol
3	697	8	664,1
4	686	9	664,9
5	664	10	664,1
6	659	11	664,5
7	662	12	659



Linear σ bonds would constrain the C–C–C angles to 60°.

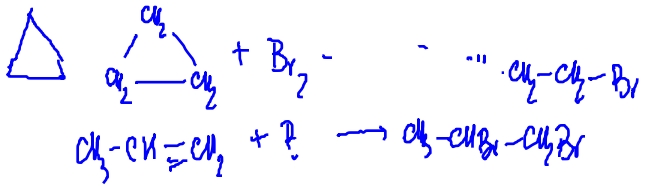
b.



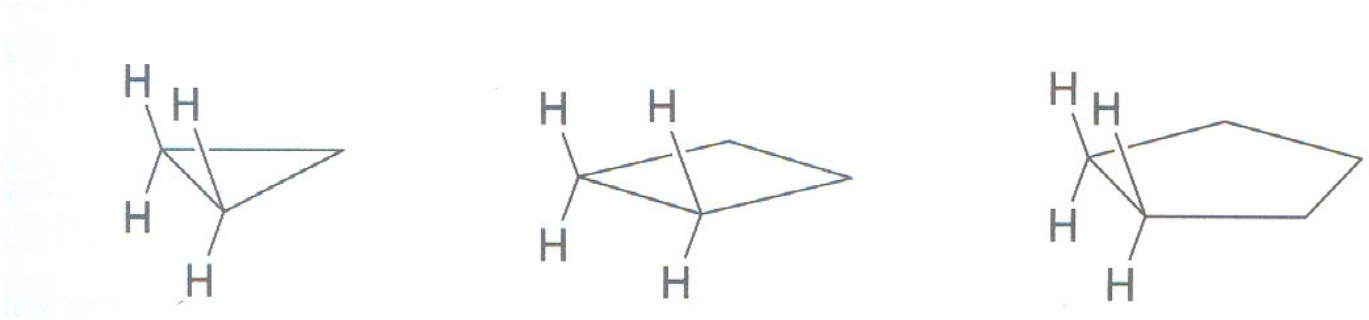
With bent σ bonds there is less strain, and each ∠C–C–C is 102°.

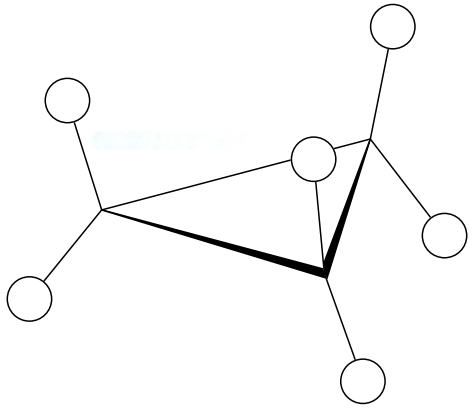
Baeyer stress - connected with bond angles

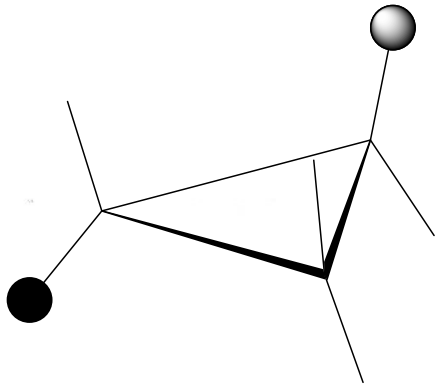
Pitzer stress - **connected with** nonbonding interactions



CONFORMATIONAL ANALYSIS

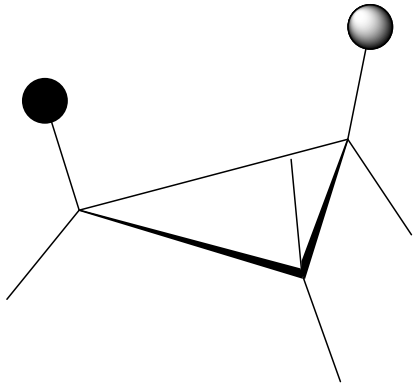






disubstituted compounds

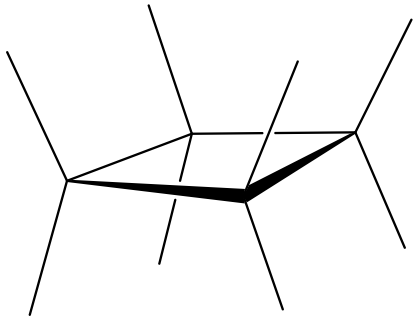
trans - isomer

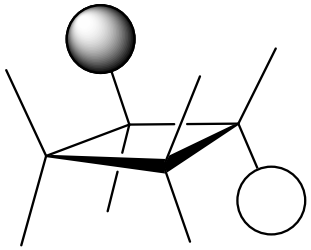


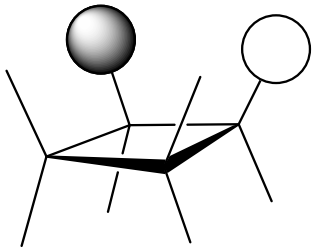
cis - isomer

In cyclic compounds we are faced to geometric isomery

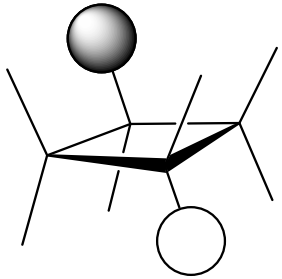
CONFORMATIONAL ANALYSIS

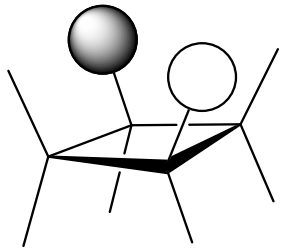






1,2 – isomers ***trans-*** ***cis-***





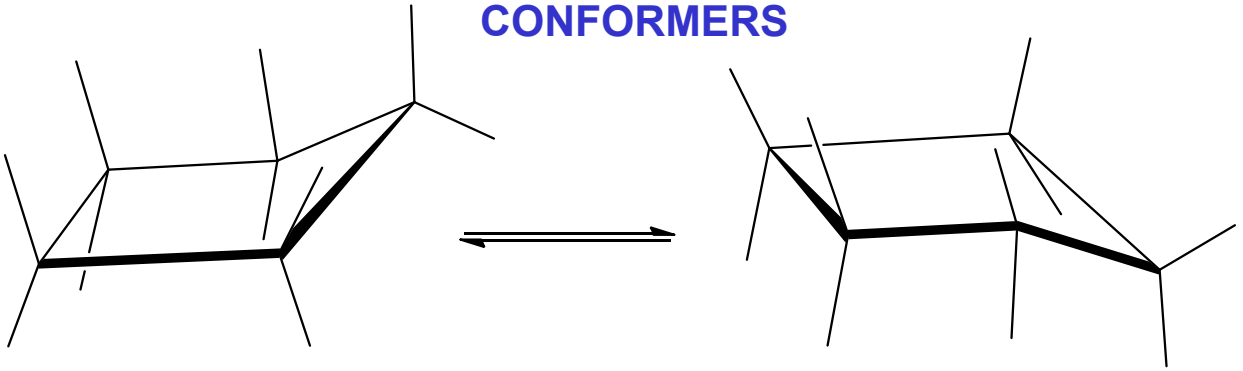
1,3 – isomers ***trans-*** ***cis-***

Number of isomers is growing:

- **position isomery**
- **geometric isomery**

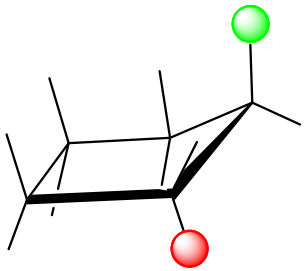
CONFORMATIONAL ANALYSIS

CONFORMERS

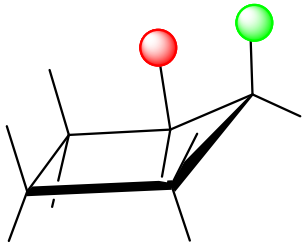


POSITION ISOMERS

geometric isomers

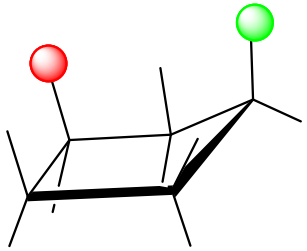


1,2 - *trans*

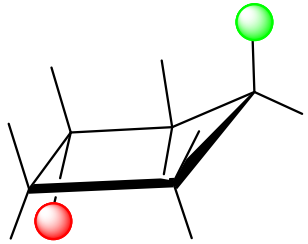


1,2 - *cis*

geometric isomers



1,3 - *cis*



1,3 - trans

In molecule of cyclopentane the strain in the molecule is released and a new possibility of rotation round bonds arose and this way transfer of one conformer to another - (envelope conformation)

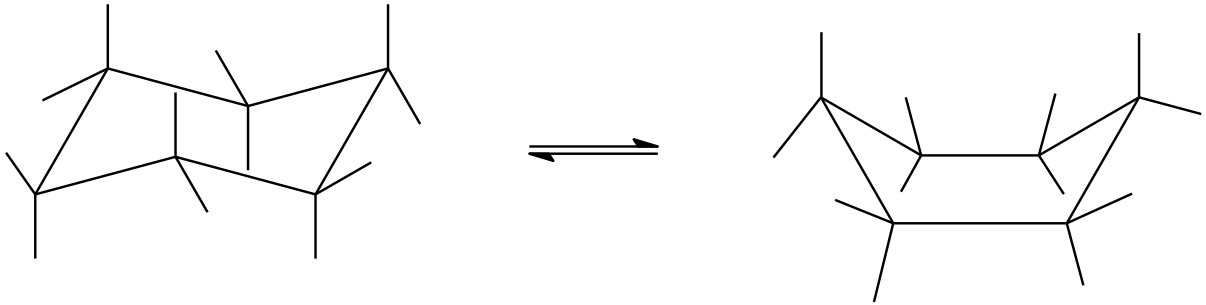
CONFORMATIONAL ANALYSIS

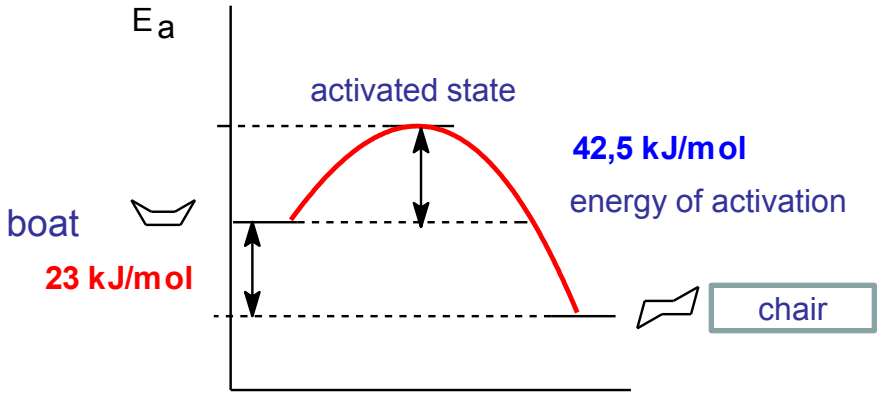
CYCLOHEXANE RING

Six-membered ring is enabling even higher motion around C-C bonds

and formation of two basic conformers - **chair and bo**

cyklohexan_zv.wrl



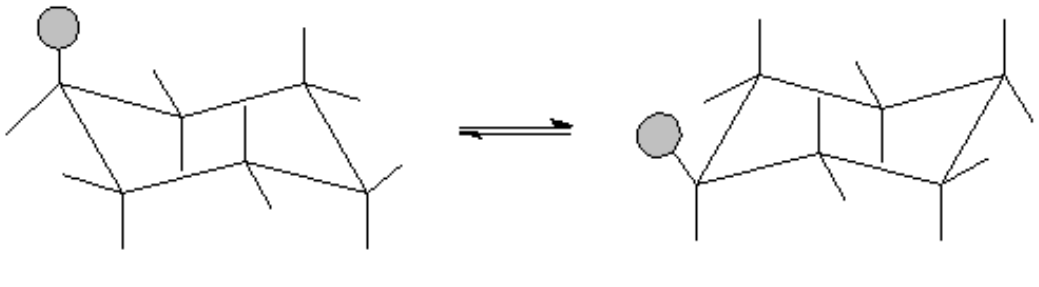


CONFORMATIONAL ANALYSIS

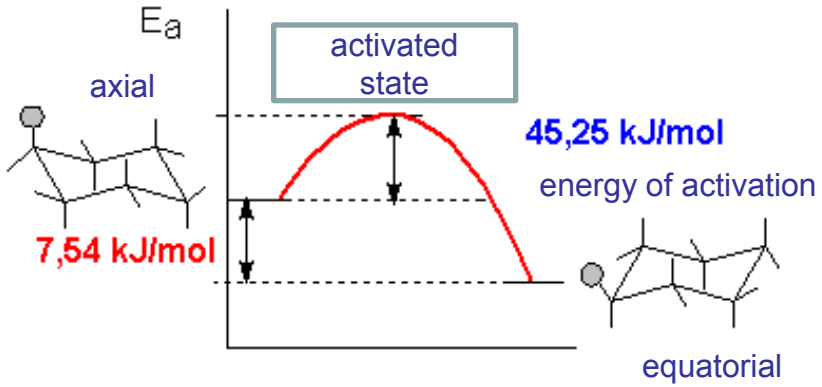
CYKLOHEXANE RING

Axial and equatorial bonds

cyklohexan_ae.wrl



● = CH_3



$$\Delta G = - RT \ln K$$

$$\ln K = - \frac{\Delta G}{RT}$$

$$\ln K = \frac{- 7{,}54}{- 8{,}31 \cdot 10^{-3} \cdot 298}$$

$$K = \frac{[e]}{[a]} \Longrightarrow [e] + [a] = 100$$

$$\ln K = 3{,}04$$

$$K = 20{,}91 = \frac{[e]}{[a]}$$

[e] = 95,43 %
[a] = 4,56 %

CONFORMATIONAL ANALYSIS

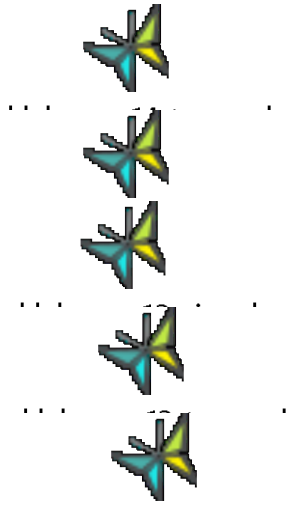
CYKLOHEXANE RING

Six-membered ring is enabling even higher motion around C-C bonds
and formation of two basic conformers - **chair and boat**

Axial and equatorial bonds

cyklohexan_ae.wrl

Existence of two geometric isomers – *cis*- a *trans*-



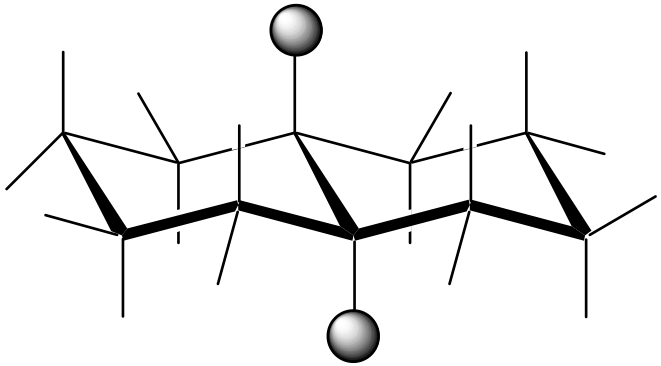
cyklohexan_12_cis.wrl

cyklohexan_12_trans.wrl

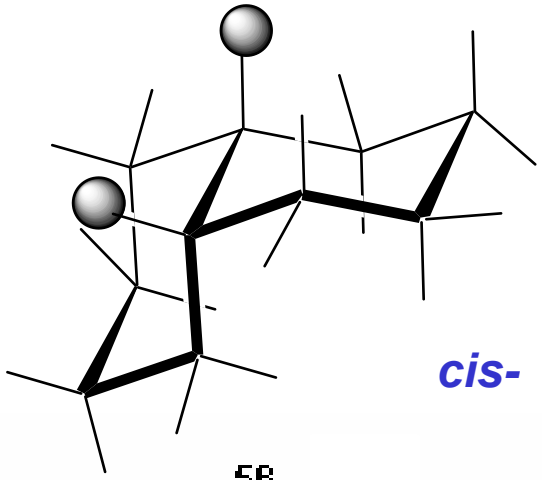
CONFORMATIONAL ANALYSIS

Polycyclic fused compounds

the rings may be fused *cis*- or *trans*-

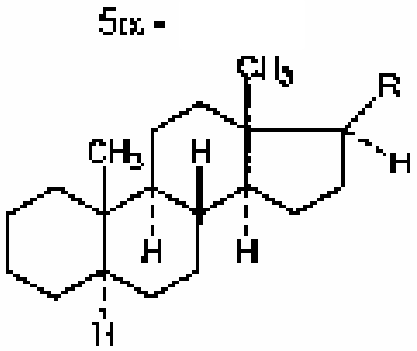


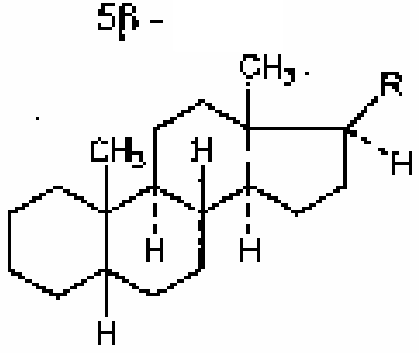
trans-



cis-

Steroids
basic skeleton





kde R = H androstan
C_2H_5 pregnan
$CH(CH_3)CH_2CH_2CH_3$ cholan
$CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$ cholestan

REACTIVITY OF ALKANES AND CYCLOALKANES

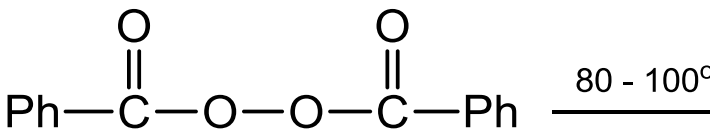
Bonds C-C and C-H are nonpolar ⇨ small reactivity in reactions with polar reagents

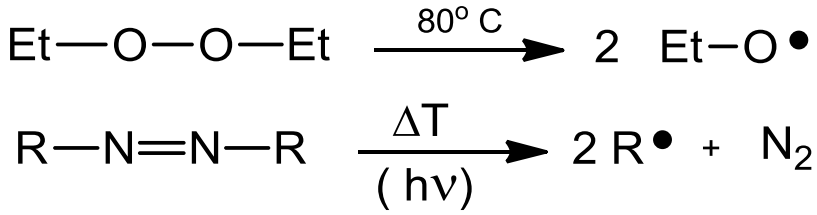
TYPICAL REACTION ARE RADICAL REACTIONS

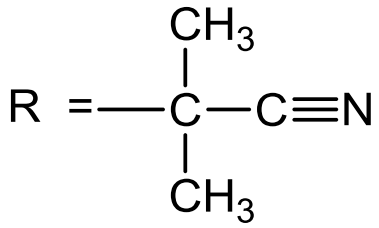
REACTIONS ARE INITIATED BY:

radicals
UV light
heat

Source of radicals are peroxides, which are decomposed by a heat







azo-bis(isobutyronitril)

REACTIVITY OF ALKANES AND CYCLOALKANES

TYPICAL REACTION – H A L O G E N A T I O N

$$CH_4 + 4\ Cl_2 \longrightarrow CCl_4 + 4\ HCl$$

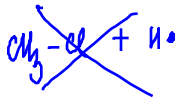
$F_2 > Cl_2 > Br_2 >>> I_2$ The realisibility of reaction depends upon the heat of reaction

Iniciation

$$Cl{-}Cl \xrightarrow{h\nu} 2\ Cl\bullet$$

Propagation

$$Cl\bullet + CH_4 \longrightarrow HCl + \bullet CH_3$$
$$\bullet CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$$



$$Cl\bullet + CH_4 \longrightarrow HCl + \bullet CH_3$$
$$\bullet CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$$

Termination

chain reaction

In the reaction mixture has disappeared one of the components

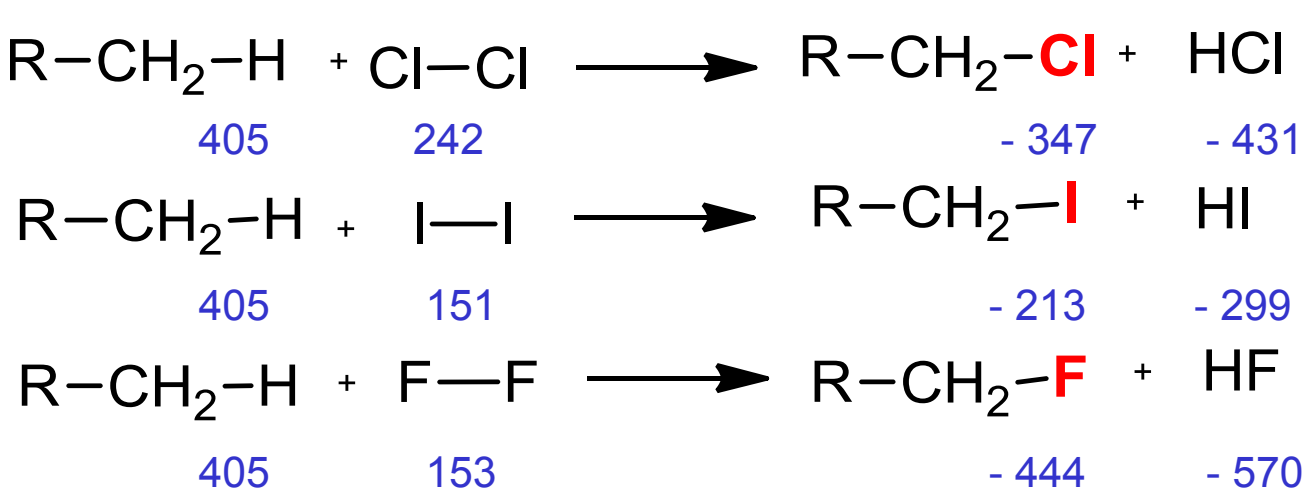
Side reactions

$$CH_3Cl + Cl\bullet \longrightarrow \bullet CH_2Cl + HCl$$
$$\bullet CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl\bullet$$

REACTIVITY OF ALKANES AND CYCLOALKANES

Energy bilance of the reaction

Energy of splitting or newly formed bonds



ΔH = -131 kJ/mol

ΔH = + 44 kJ/mol

ΔH = - 456 kJ/mol

strongly exothermic reaction

Bond energy of C – C = 346 kJ/mol

REACTIVITY OF ALKANES AND CYCLOALKANES

SELECTIVITY OF REACTIONS

energy of different way bonded hydogen atoms is different

CH_3-CH_3

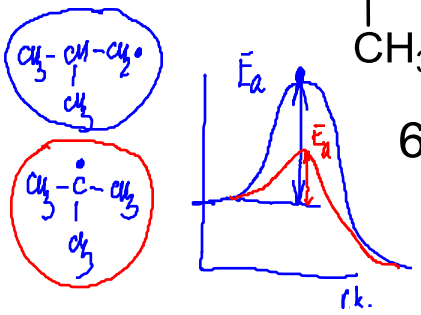
$CH_3-CH_2-CH_3$ $\xrightarrow{Cl_2 / 25^o\ C}$ $CH_3-CH_2-CH_2-Cl$ + $CH_3-\underset{Cl}{CH}-CH_3$

45% 55%

ratio H 3 : 1

yield 1 : 3,66

$CH_3-\underset{CH_3}{CH}-CH_3$ $\xrightarrow{Cl_2 / 25^o\ C}$ $CH_3-\underset{CH_3}{CH}-CH_2-Cl$ + $CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3$



63% 37%

ratio H 9 : 1

yield 1 : 5,28

$CH_3-\underset{CH_3}{CH}-CH_3$ $\xrightarrow{Br_2 / 25^o\ C}$ $CH_3-\underset{CH_3}{CH}-CH_2-Br$ + $CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3$

1% 99%

ratio H 9 : 1

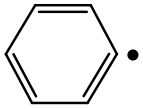
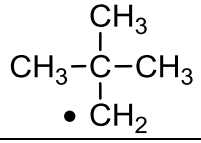
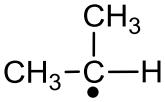
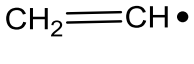
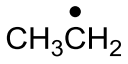
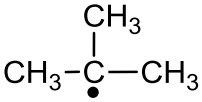
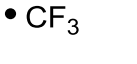
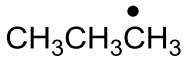
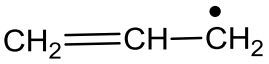
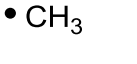
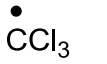
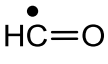
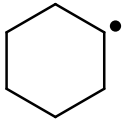
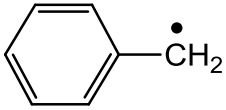
yield 1 : 99

REACTIVITY OF ALKANES AND CYCLOALKANES

SELECTIVITY OF REACTIONS

is depending upon stability of formed radicals

Energy of dissotiation of different bonds R-H (Stability of radicals)

	kcal/mol		kcal/mol		kcal/mol
	110		100		95
	> 108		98		92
	106		98		89
	104		96		87
	101		95		85