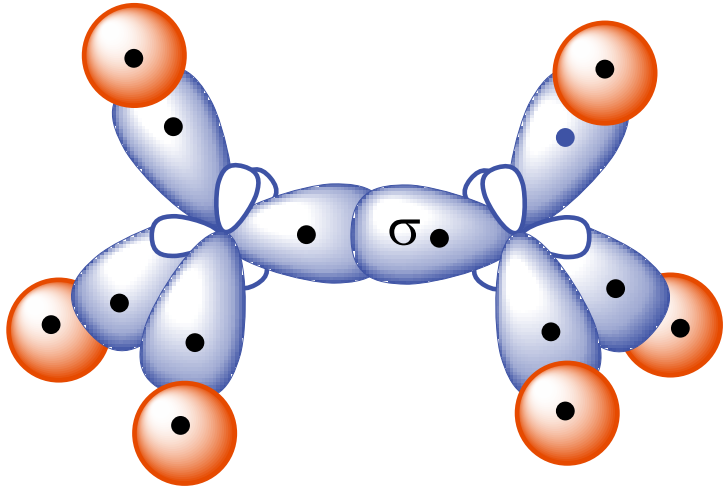
Alkany a cykloalkany

Alkany a cykloalkany: hlavní složky zemního plynu a ropy (zdroj energie, paliv).
Nasycené alkany a cykloalkany mají pouze ***jednoduché vazby*** uhlík-vodík (C-H) a uhlík-uhlík (C-C).

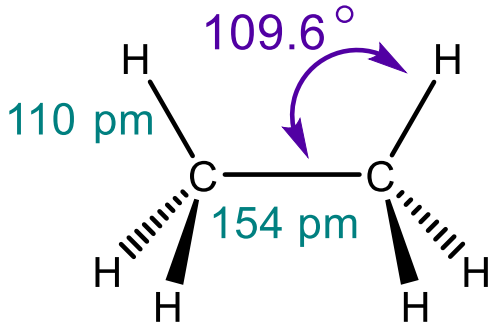
sp^3

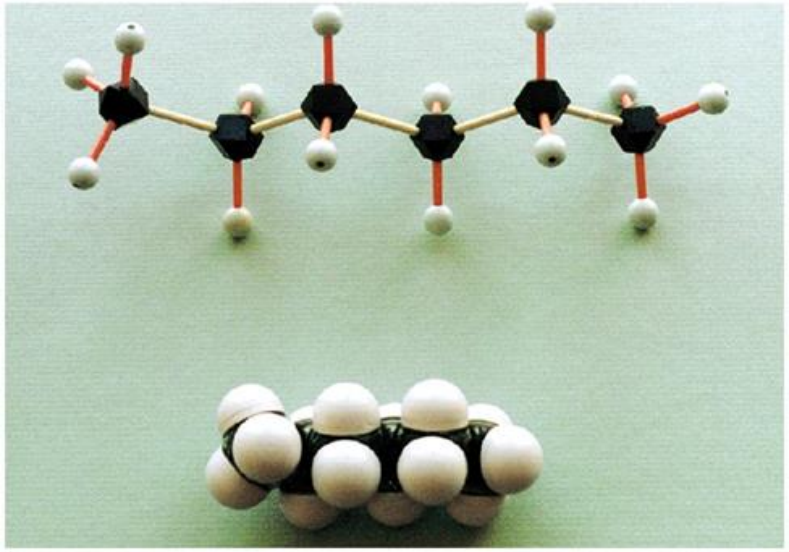


Alkany mají obecný molekulární vzorec:

C_nH_{2n+2},

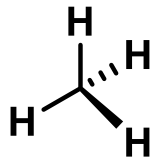
kde n je počet atomů uhlíku.



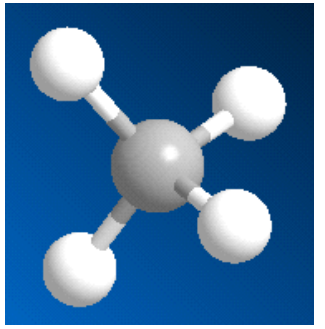


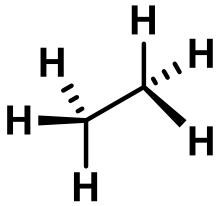
Struktura alkanů je pravidelná. Uhlíkové atomu jsou tetraedrální v hybridizaci **sp³**

(vazebné úhly cca. 109°), délka vazby C-C je ~1.54 Å a C-H vazby ~ 1.10 Å.

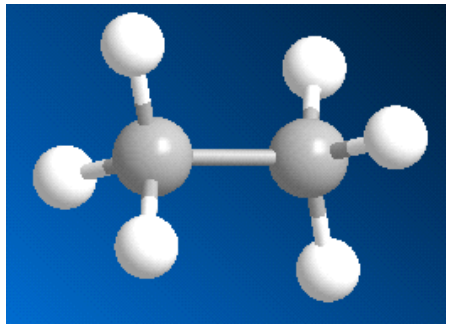


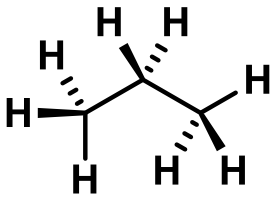
CH_4 methan



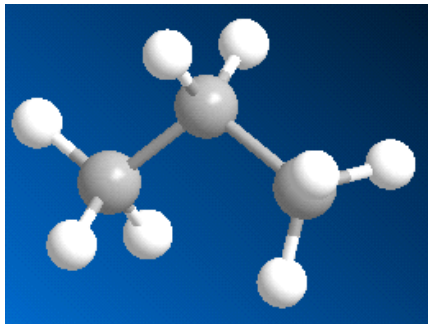


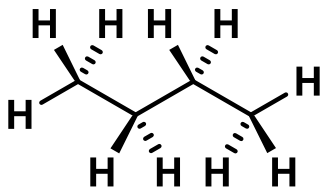
C_2H_6 ethan



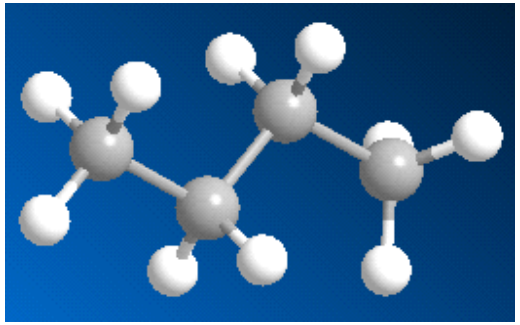


C_3H_8 propan



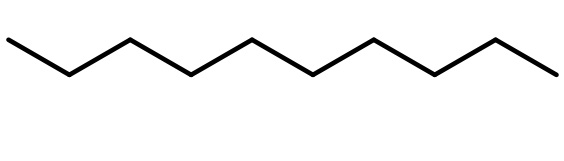


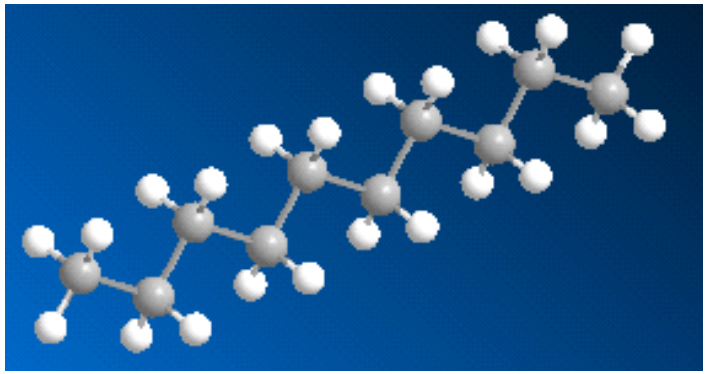
C_4H_{10} butan



lineární

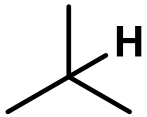
dekan $C_{10}H_{22}$

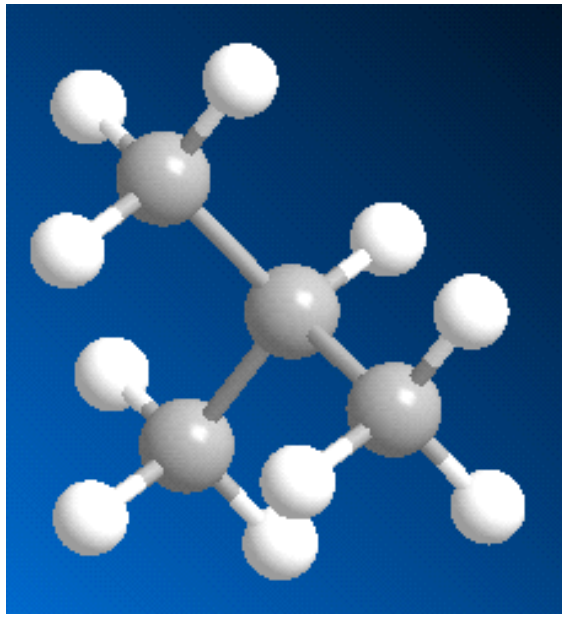




rozvětvený

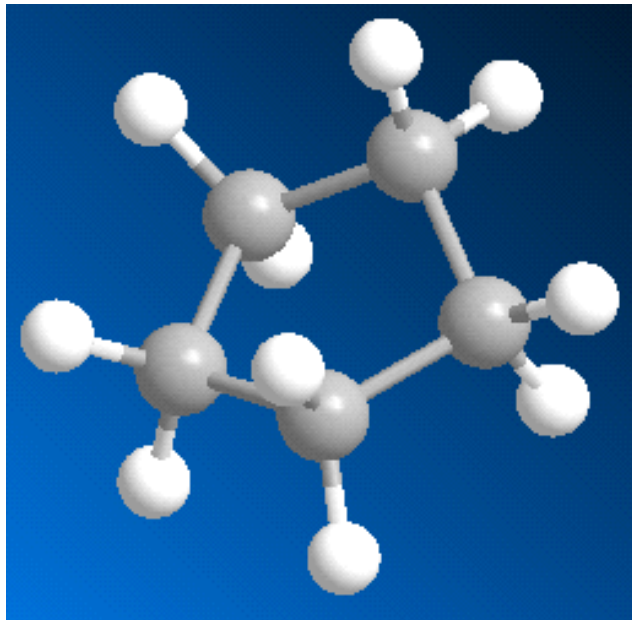
isobutan C_4H_{10}





cykloalkan

cyklopentan



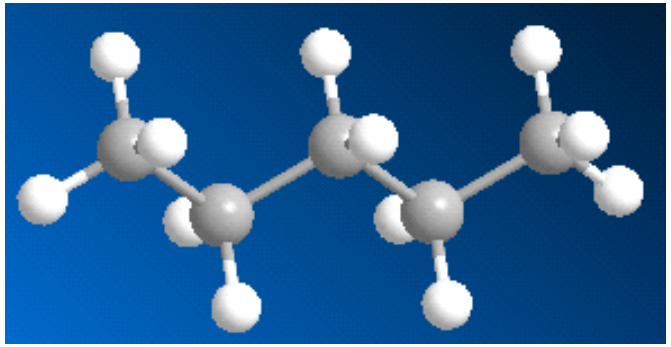
Lineární a rozvětvené alkany – Izomery

TABLE 2-4
Number of Possible Isomeric Alkanes, C_nH_{2n+2}

n	Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319

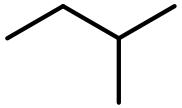
$CH_3CH_2CH_2CH_2CH_3$

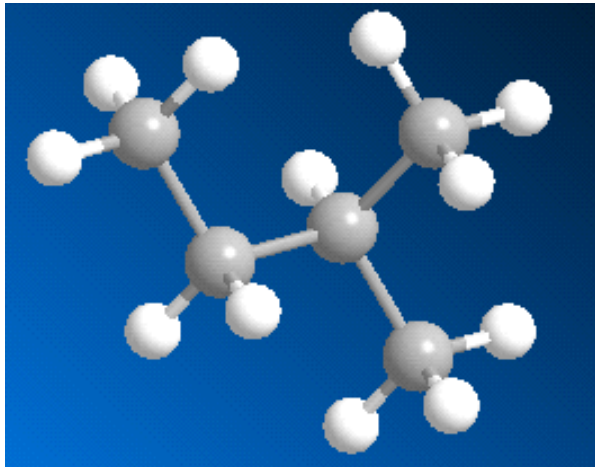
pentan



$CH_3CH(CH_3)CH_2CH_3$

2-methylbutan
(Isopentan)





$CH_3C(CH_3)_2CH_3$

2,2-dimethylpropan
(neopentan)

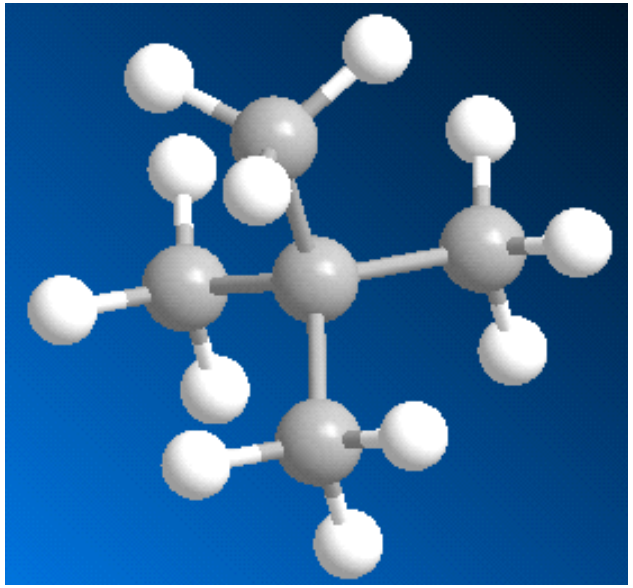


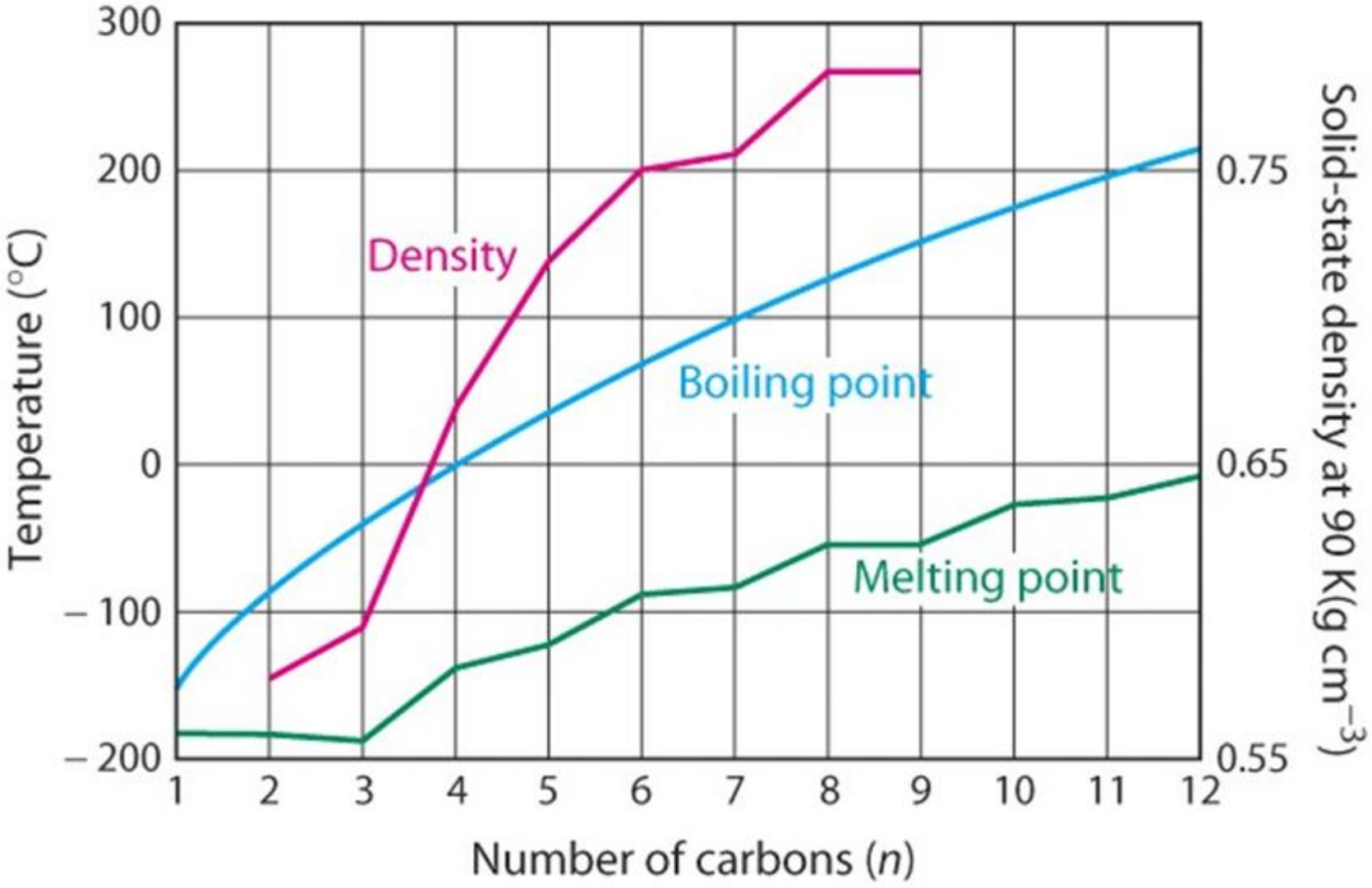
TABLE 2-5 Names and Physical Properties of Straight-Chain Alkanes, C_nH_{2n+2}

n	Name	Formula	Boiling point (°C)	Melting point (°C)	Density at 20°C (g ml^{-1})
1	Methane	CH_4	−161.7	−182.5	0.466 (at −164°C)
2	Ethane	CH_3CH_3	−88.6	−183.3	0.572 (at −100°C)
3	Propane	$CH_3CH_2CH_3$	−42.1	−187.7	0.5853 (at −45°C)
4	Butane	$CH_3CH_2CH_2CH_3$	−0.5	−138.3	0.5787
5	Pentane	$CH_3(CH_2)_3CH_3$	36.1	−129.8	0.6262
6	Hexane	$CH_3(CH_2)_4CH_3$	68.7	−95.3	0.6603
7	Heptane	$CH_3(CH_2)_5CH_3$	98.4	−90.6	0.6837
8	Octane	$CH_3(CH_2)_6CH_3$	125.7	−56.8	0.7026
9	Nonane	$CH_3(CH_2)_7CH_3$	150.8	−53.5	0.7177
10	Decane	$CH_3(CH_2)_8CH_3$	174.0	−29.7	0.7299

TABLE 2-5 Names and Physical Properties of Straight-Chain Alkanes, C_nH_{2n+2}

n	Name	Formula	Boiling point (°C)	Melting point (°C)	Density at 20°C (g ml^{-1})
11	Undecane	$CH_3(CH_2)_9CH_3$	195.8	−25.6	0.7402
12	Dodecane	$CH_3(CH_2)_{10}CH_3$	216.3	−9.6	0.7487
13	Tridecane	$CH_3(CH_2)_{11}CH_3$	235.4	−5.5	0.7564
14	Tetradecane	$CH_3(CH_2)_{12}CH_3$	253.7	5.9	0.7628
15	Pentadecane	$CH_3(CH_2)_{13}CH_3$	270.6	10	0.7685
16	Hexadecane	$CH_3(CH_2)_{14}CH_3$	287	18.2	0.7733
17	Heptadecane	$CH_3(CH_2)_{15}CH_3$	301.8	22	0.7780
18	Octadecane	$CH_3(CH_2)_{16}CH_3$	316.1	28.2	0.7768
19	Nonadecane	$CH_3(CH_2)_{17}CH_3$	329.7	32.1	0.7855
20	Icosane	$CH_3(CH_2)_{18}CH_3$	343	36.8	0.7886

Fyzikální vlastnosti alkanů sledují predikovatelné trendy



Alkylová skupina (alkyl) je vytvořena formálním odstraněním vodíku z alkanu. Je pojmenována jako alkyl (přípona –**yl**).

CH_3- methyl; CH_3CH_2- ethyl; $CH_3CH_2CH_2$- propyl

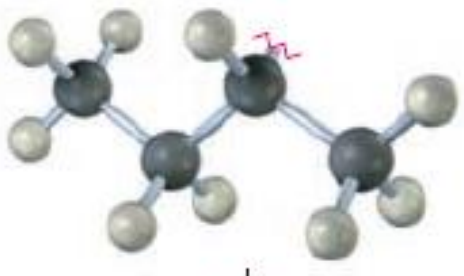
Doplňující předpony jsou : *sec*- (nebo *s*-) pro sekundární a *tert*- (nebo *t*-) pro terciární. Sekundární uhlík je připojen k dalším dvěma uhlíkům, zatímco terciární ke třem uhlíkům a kvartérní ke čtyřem uhlíkům.

$CH_3CH_2CH_2CH_3$

Butane

$CH_3CH_2CH_2CH_2$–

Butyl



$CH_3CH_2CHCH_3$

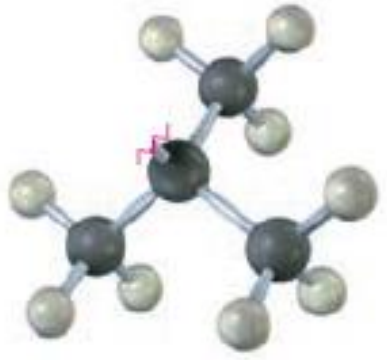
***sec*-Butyl**

CH_3CHCH_3 (CH_3 above)

Isobutane

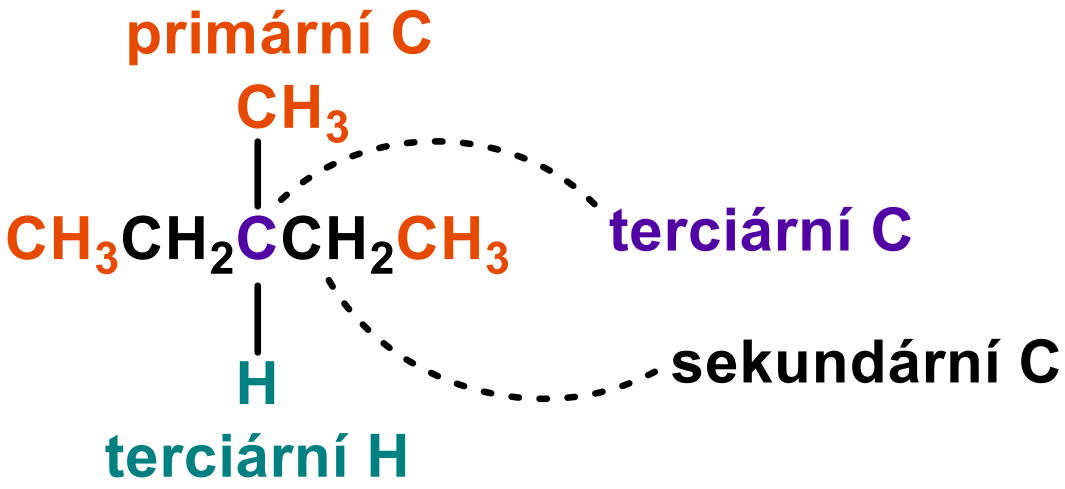
CH_3CHCH_2– (CH_3 above)

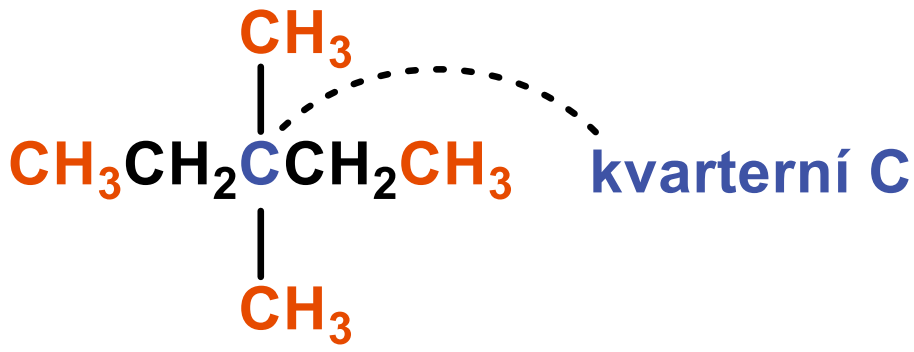
Isobutyl



$CH_3C(CH_3)_2$–

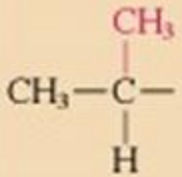
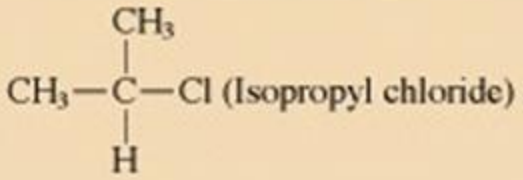
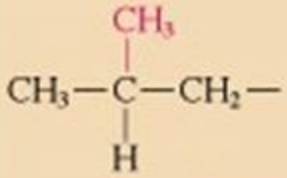
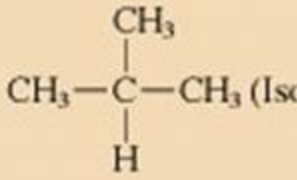
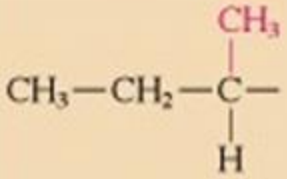
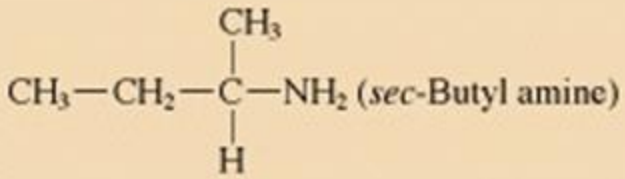
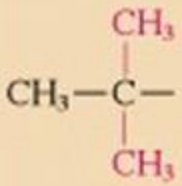
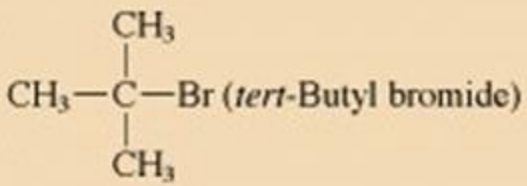
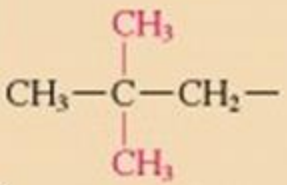
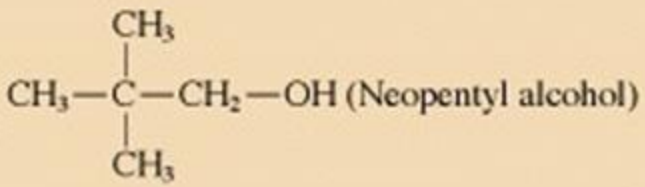
***tert*-Butyl**


primární C
CH3
CH3CH2CCH2CH3
terciární C
sekundární C
H
terciární H


CH3
CH3CH2CCH2CH3
kvarterní C
CH3

Vybrané rozvětvené alkyly

TABLE 2-6 Branched Alkyl Groups

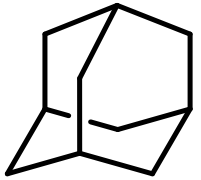
Structure	Common name	Example of common name in use	Systematic name	Type of group
	Isopropyl	 (Isopropyl chloride)	1-Methylethyl	Secondary
	Isobutyl	 (Isobutane)	2-Methylpropyl	Primary
	*sec*-Butyl	 (*sec*-Butyl amine)	1-Methylpropyl	Secondary
	*tert*-Butyl	 (*tert*-Butyl bromide)	1,1-Dimethylethyl	Tertiary
	Neopentyl	 (Neopentyl alcohol)	2,2-Dimethylpropyl	Primary

Výskyt alkanů v přírodě a jejich vlastnosti

Ropa je složitá směs organických sloučenin, z nichž větší část je tvořena alkany a cykloalkany. Složení ropy je závislé na místě původu.

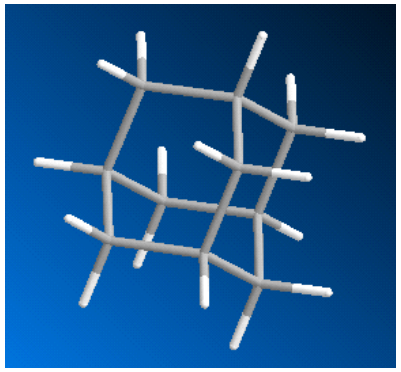
https://cs.wikipedia.org/wiki/Ropa

Alkany se nacházejí i přírodě a jsou produkovány některými rostlinami: cykloalkany a heptan tvoří hlavní složku terpenických silic.

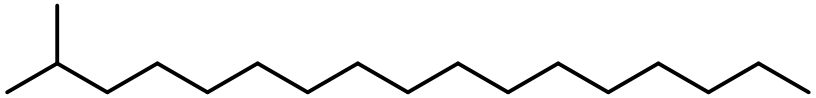


adamantan

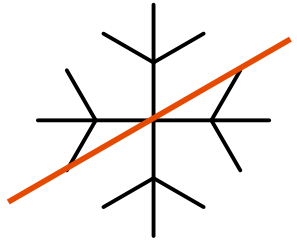
tricyklo[3,3,1,1^{3,7}]dekan



Stanislav Landa 1932, izolace z hodonínské ropy.



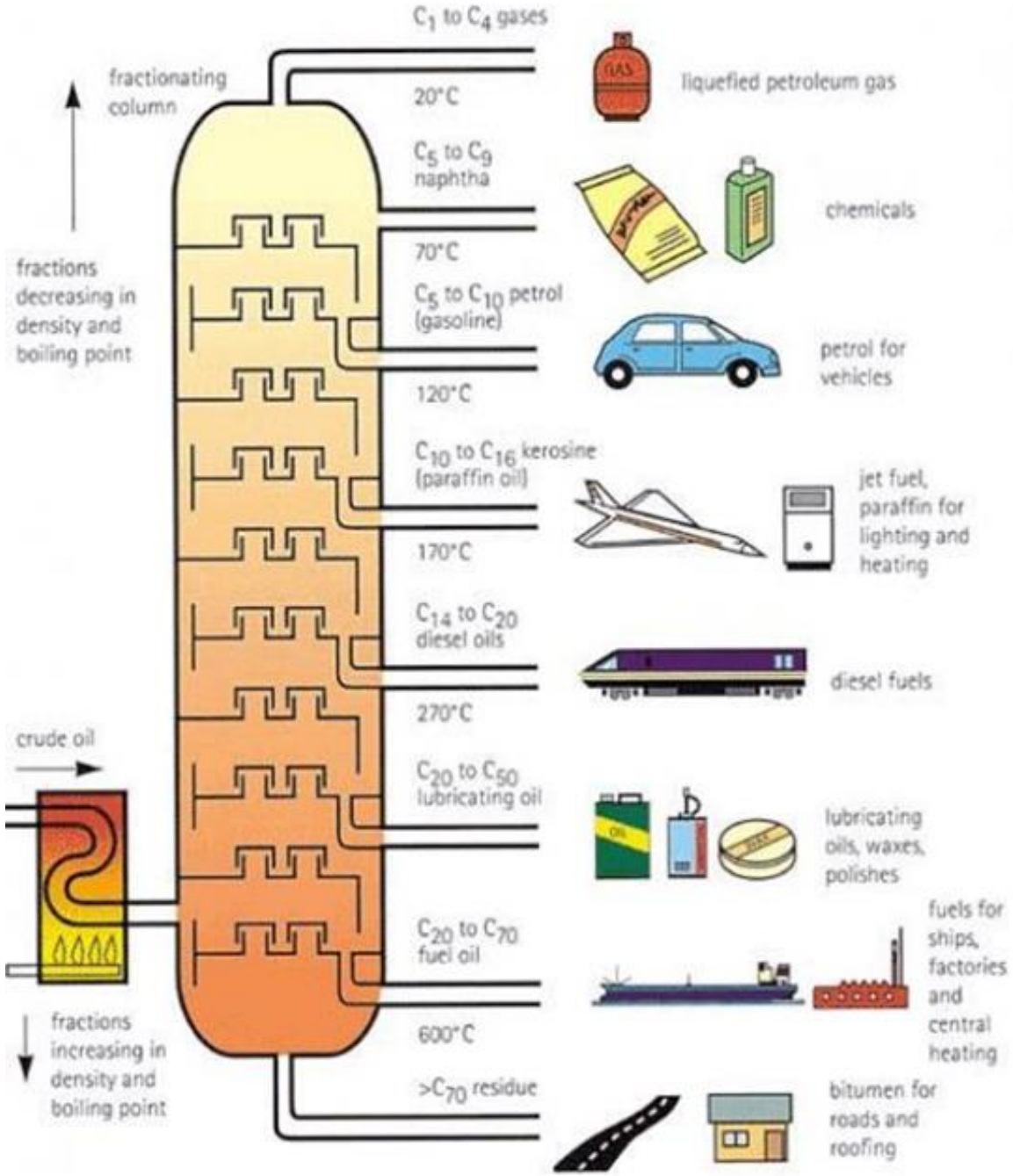
2-methylheptadekan

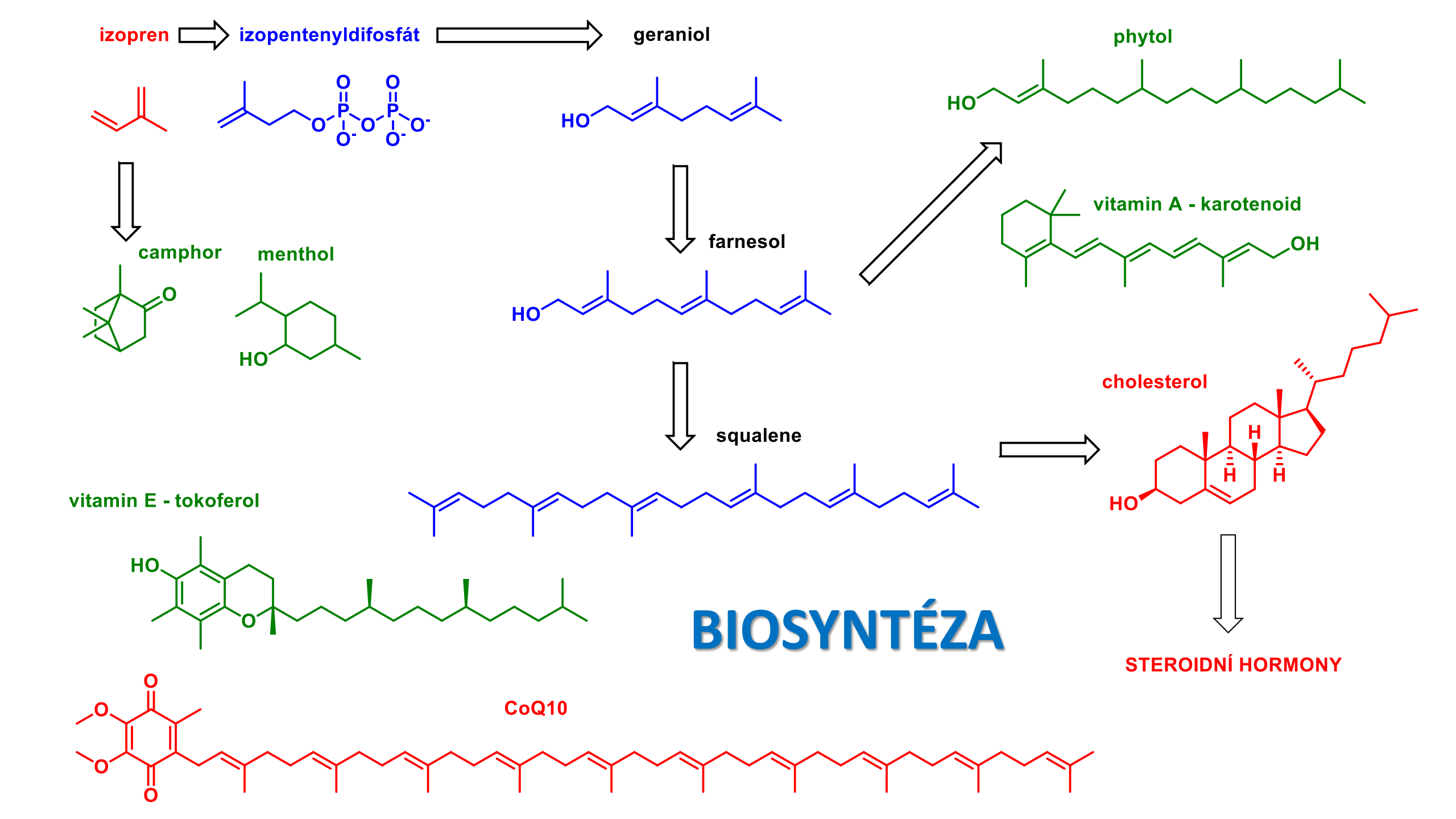


neexistuje stérické bránění

3,3-di-*tert*-butyl-2,2,4,4-tetramethylpentan

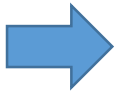
Destilace ropy



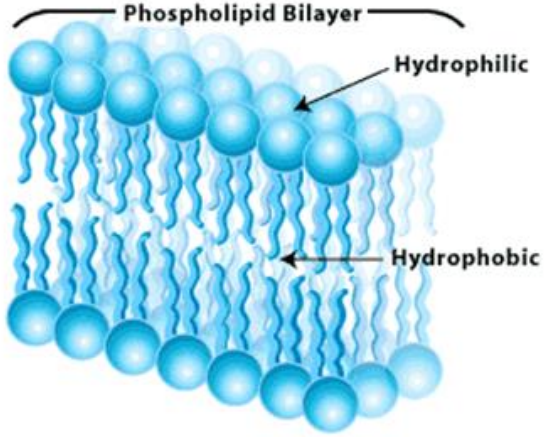

izopren
izopentenyldifosfát
geraniol
phytol
camphor
menthol
farnesol
vitamin A - karotenoid
squalene
cholesterol
vitamin E - tokoferol
BIOSYNTÉZA
STEROIDNÍ HORMONY
CoQ10

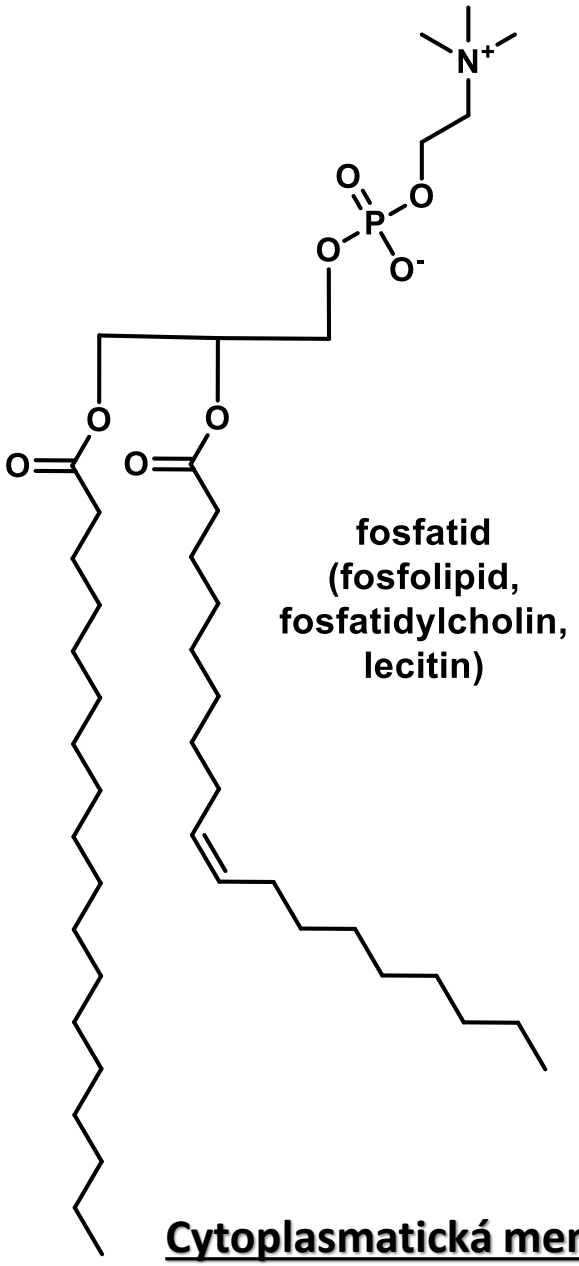
Vosky

Vyšší *n*-alkany jsou součástí nebo výhradní složkou přírodních vosků a tvoří ochrannou vrstvu na rostlinách: $C_{27}H_{56}$ a $C_{29}H_{60}$ (jablka), $C_{29}H_{60}$ (zelí, brokolice) a $C_{31}H_{64}$ (tabákové listy).

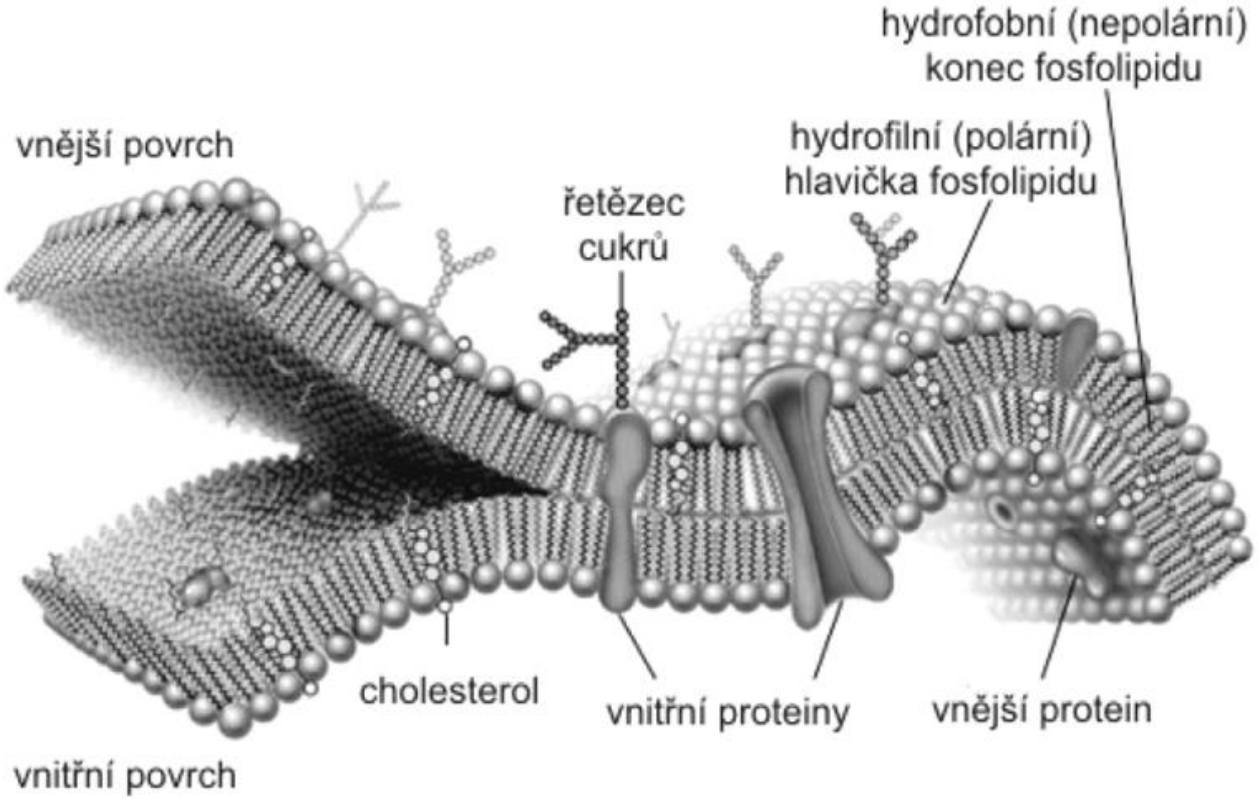


Hydrofobicita alkylových řetězců – biologické membrány





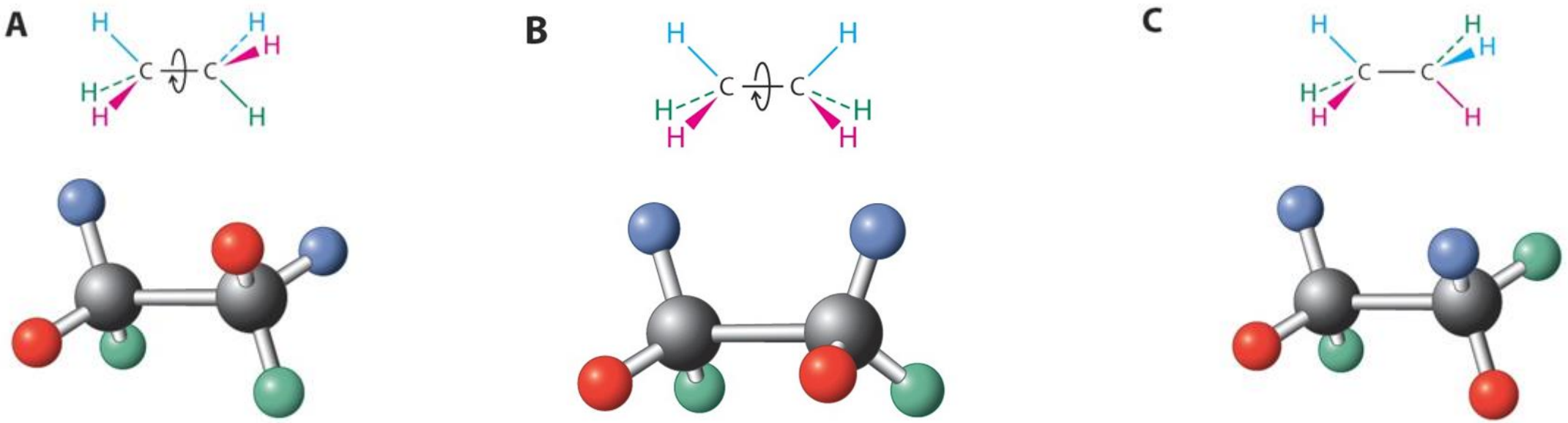
fosfatid (fosfolipid, fosfatidylcholin, lecitin)



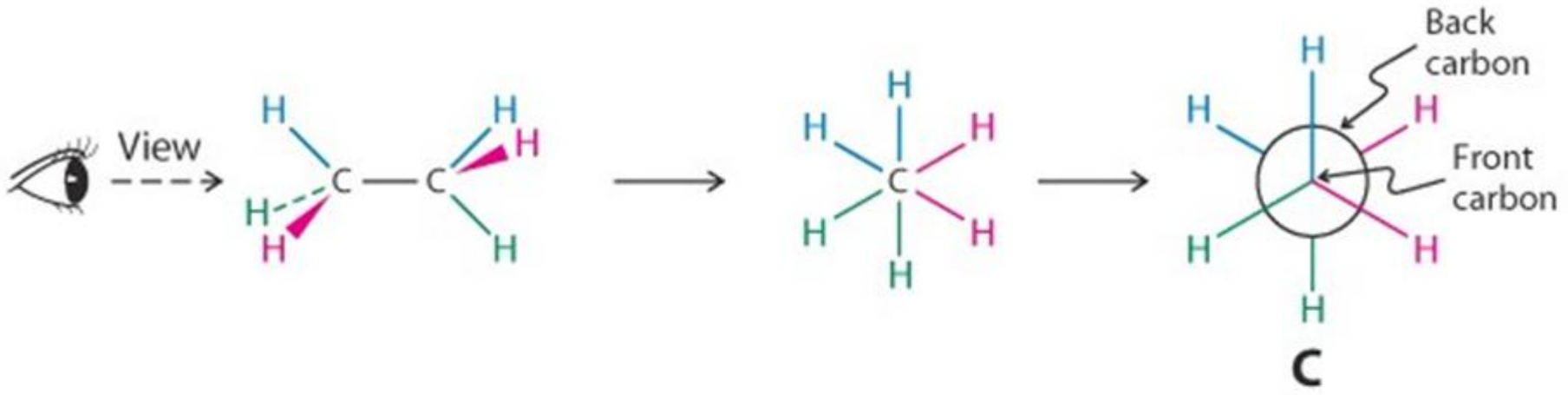
Cytoplasmatická membrána - model fluidní mozaiky (Chem. Listy *109*, 166–175 (2015))

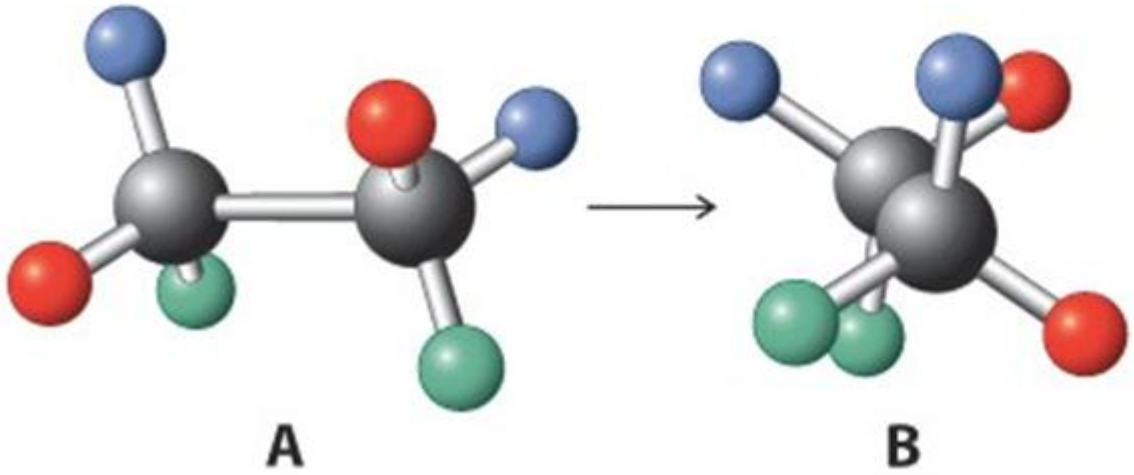
Rotace kolem jednoduché vazby: konformace

Rotační bariera kolem C-C vazby ethanu je 2.9 kcal/mol. Toto relativně nízké množství energie je k dispozici za pokojové teploty v důsledku molekulárních srážek, a proto se uvádí, že kolem C-C vazby ethanu je volná rotace.



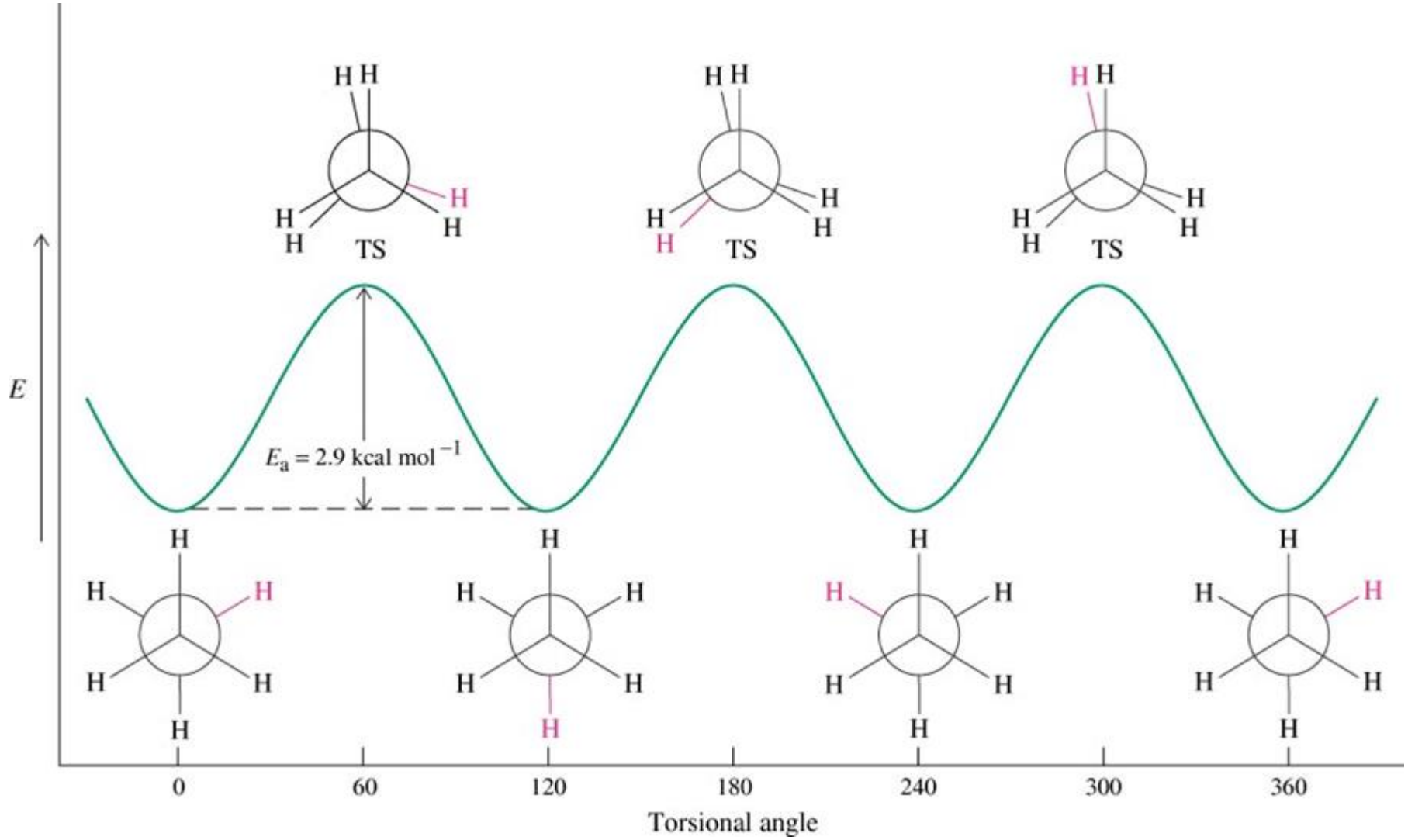
Newmanova projekce konformací ethanu.



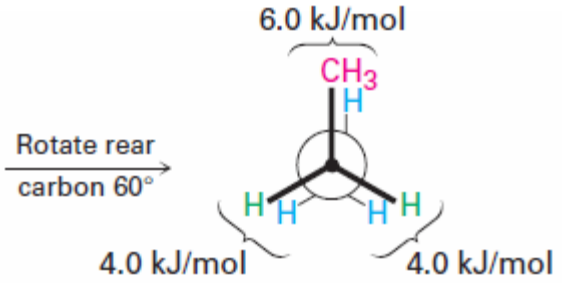


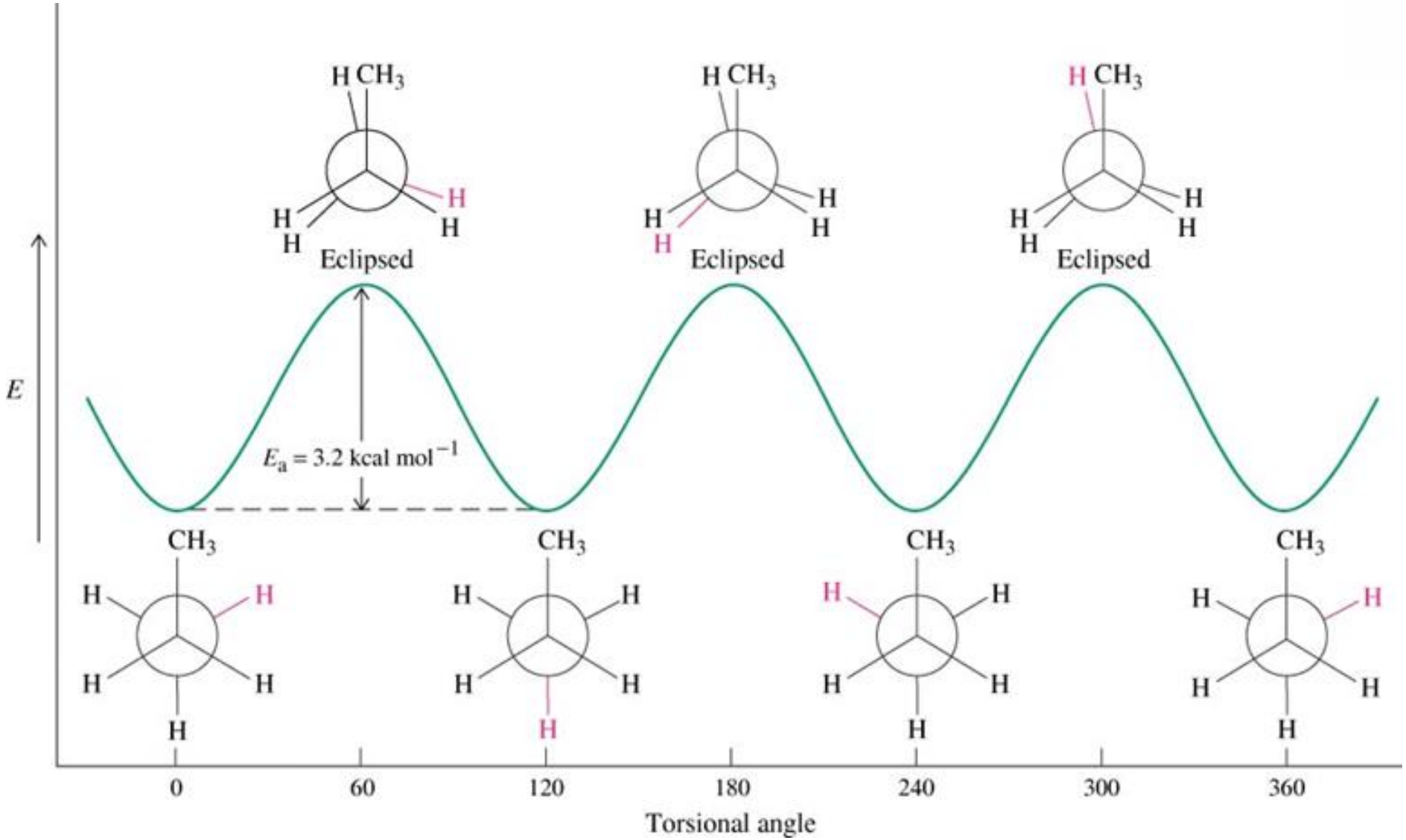
Rotamery ethanu mají různou potenciální energii.

Nejnižší energii má střídavá konformace a nejvyšší zákrytová konformace (cca. 2.9 kcal/mole vyšší).

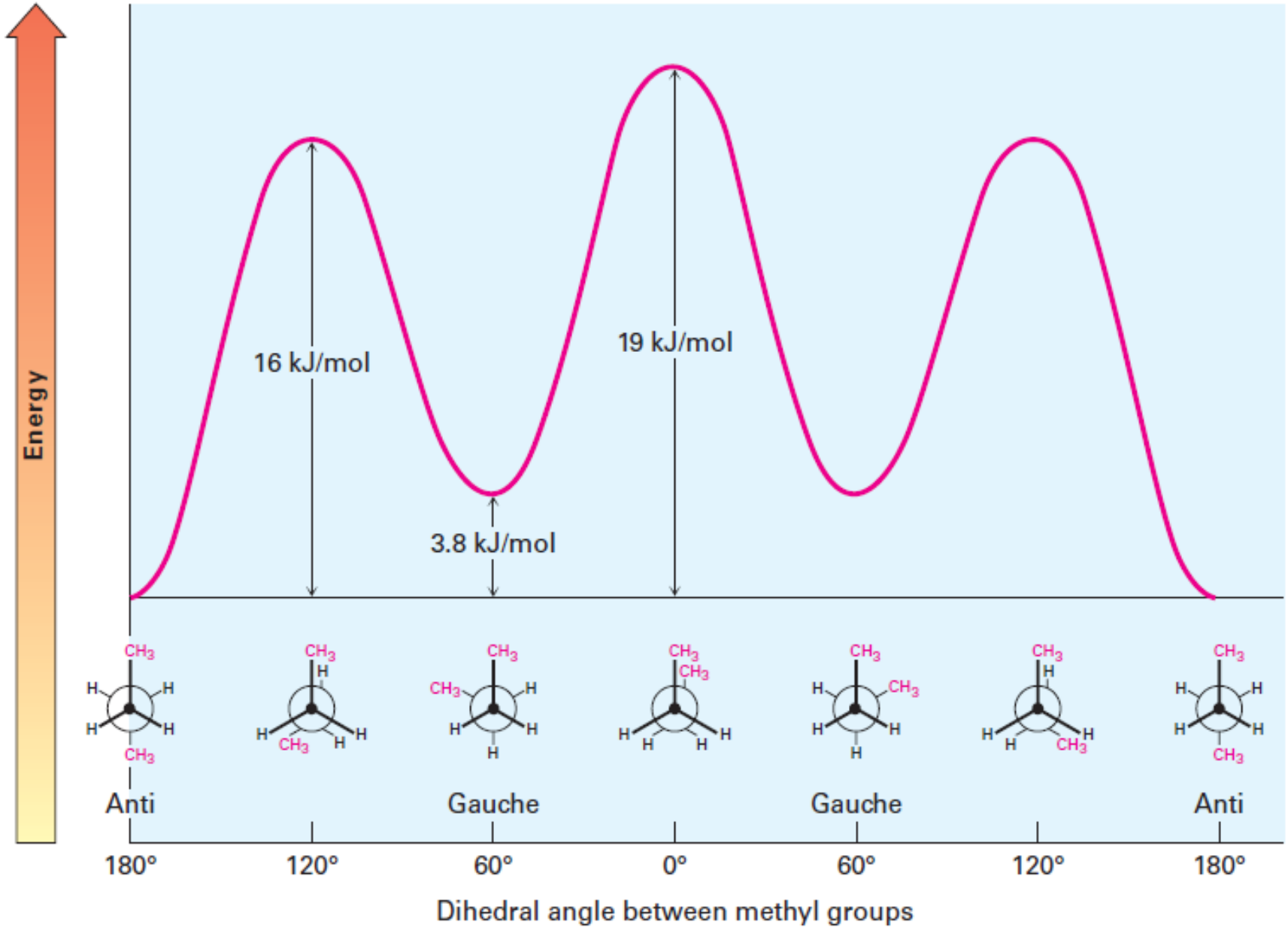


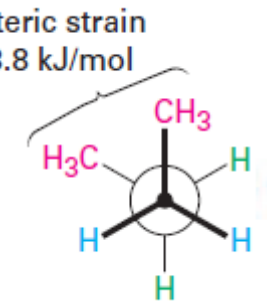
Konformace propanu

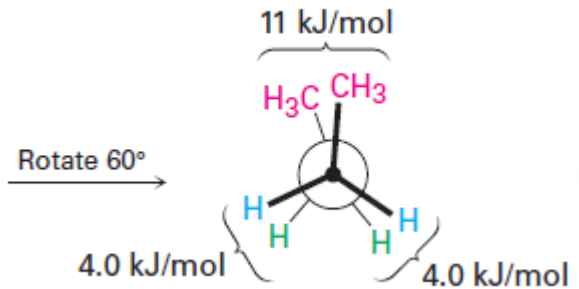




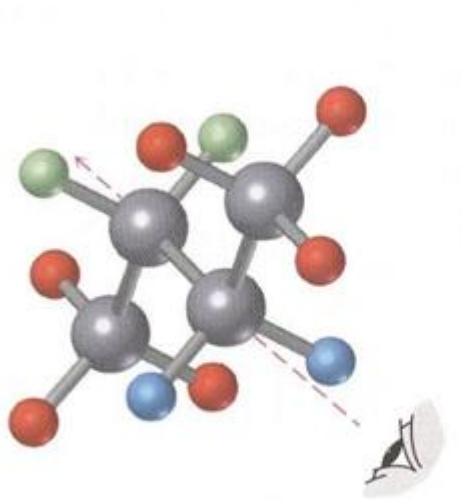
Konformace butanu



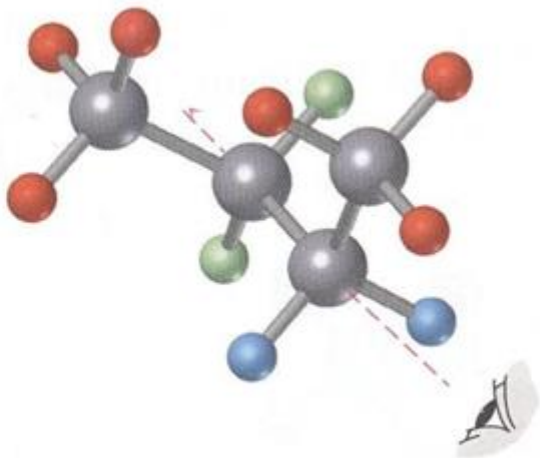




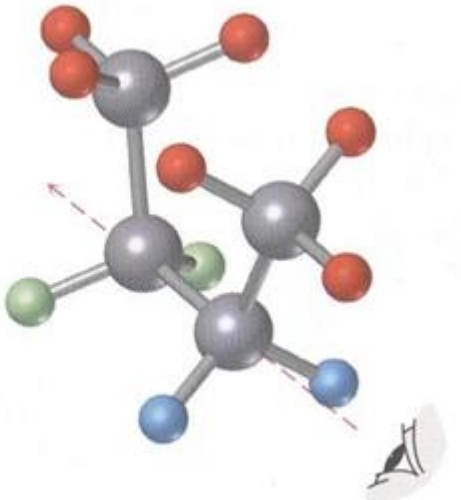
Konformace butanu



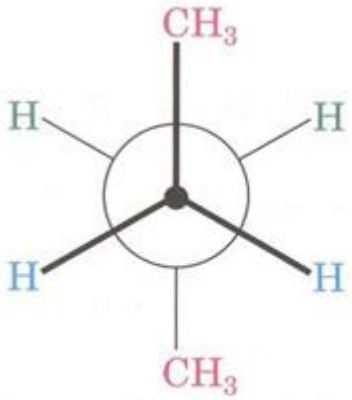
pozorovatel



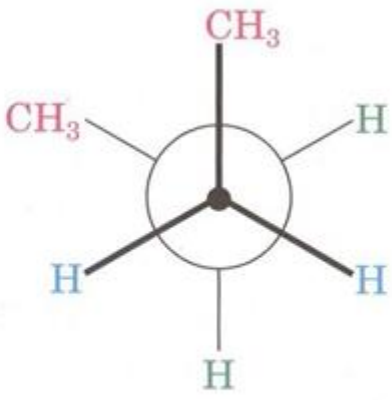
pozorovatel



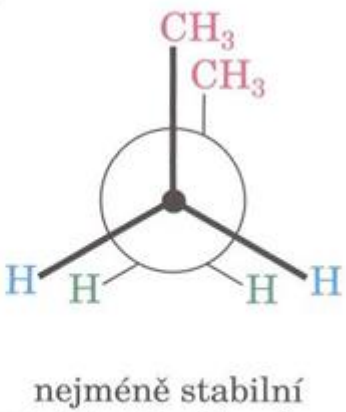
pozorovatel



antiperiplanární



synklinální



nejméně stabilní
synperiplanární konformace

Reakce alkanů

Alkany jsou málo reaktivní, reagují především radikálovým mechanismem: **oxidace** (O_2, tvorba peroxidů), **halogenace** (X_2, NBS, SO_2Cl_2), sulfochlorace (Cl_2 a SO_2) a nitrace (N_2O_4 a HNO_3).

Oxidace (spalování):

$$CH_4 + 3O_2 \longrightarrow CO_2 + 2H_2O \quad 892\ kJ/mol$$

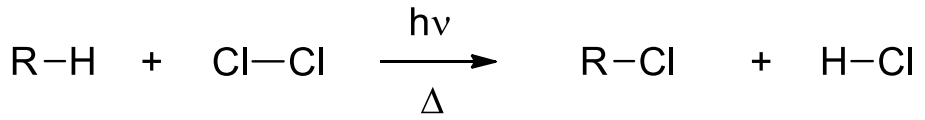
$$C_4H_{10} + 6.5O_2 \longrightarrow 4CO_2 + 5H_2O \quad 2883\ kJ/mol$$

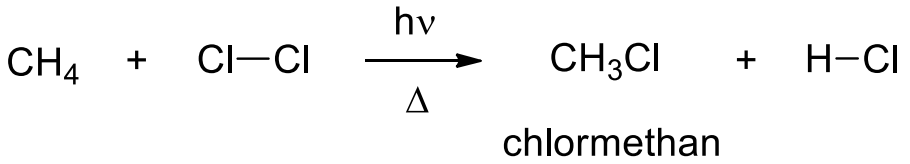
$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

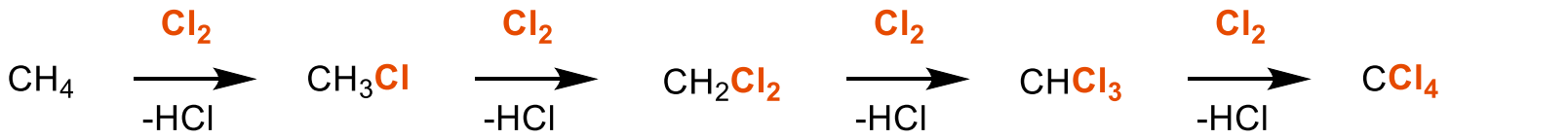
$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

$$CH_4 + 2O_2 \longrightarrow \underset{\text{formaldehyd}}{CH_2O} + H_2O$$

Halogenace alkanů:





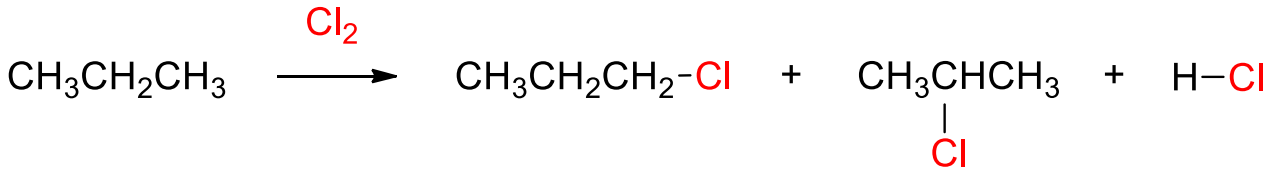


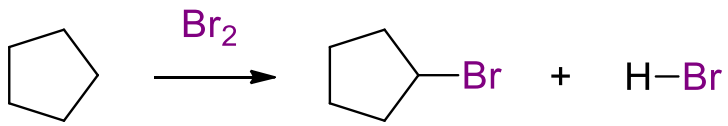
chlormethan
b.v. -24.5°C

dichlormethan
b.v. 40°C

trichlormethan
b.v. 61.7°C
(chloroform)

tetrachlormethan
b.v. 75.6°C



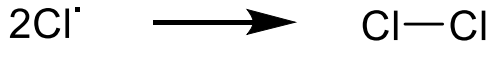


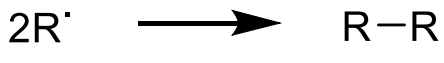
Mechanismus halogenace:

Iniciace

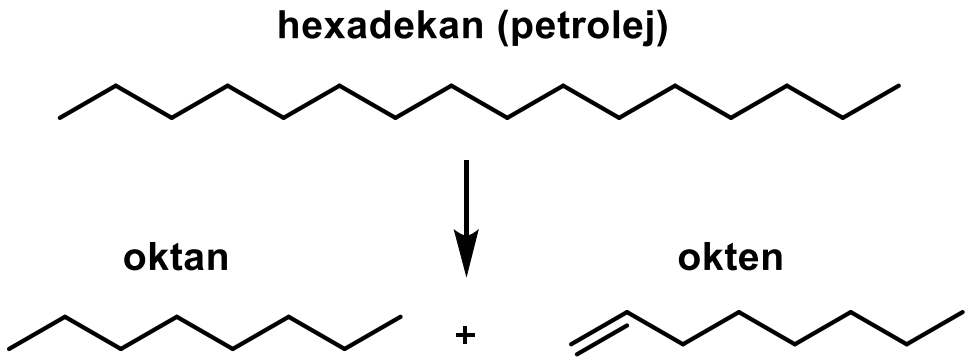
Propagace

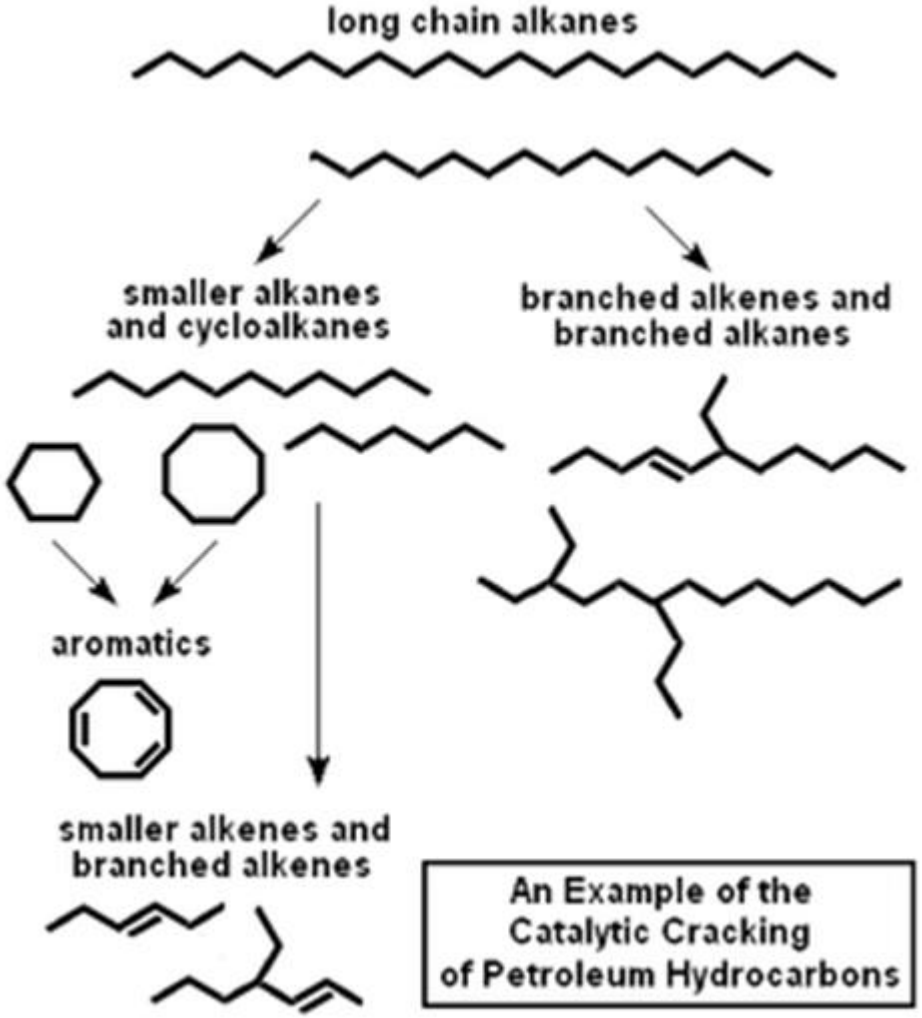
Terminace





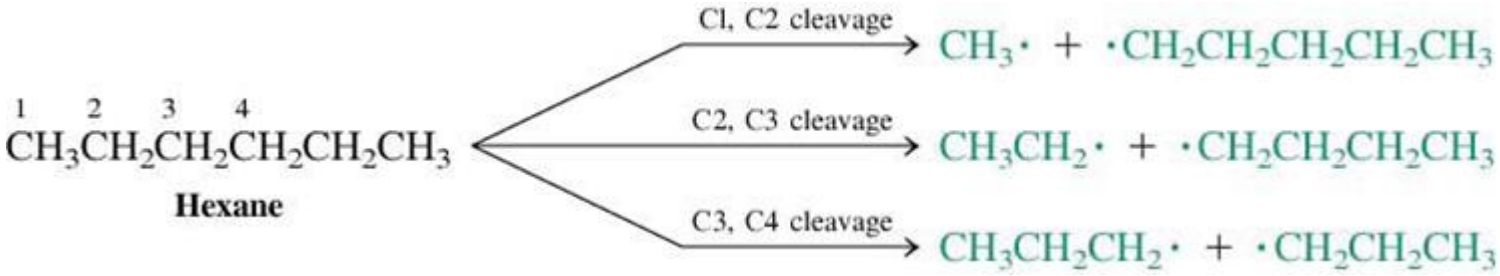
Krakování ropy - výroba benzínu



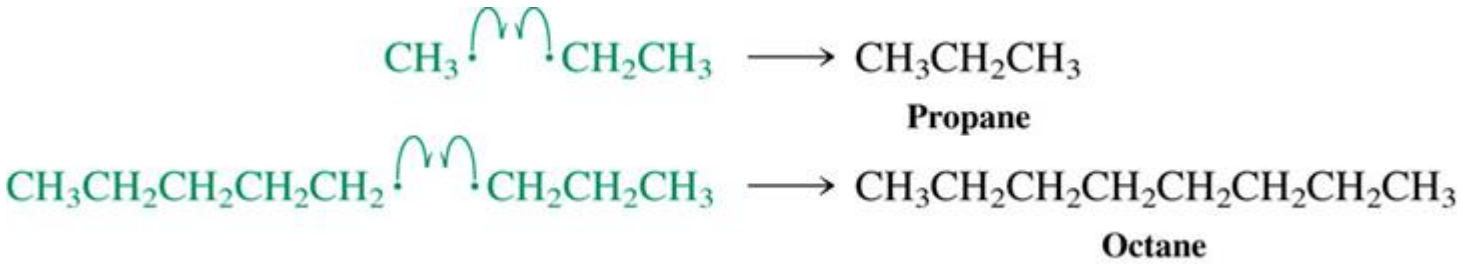


Krakování uhlovodíků – radikálová reakce

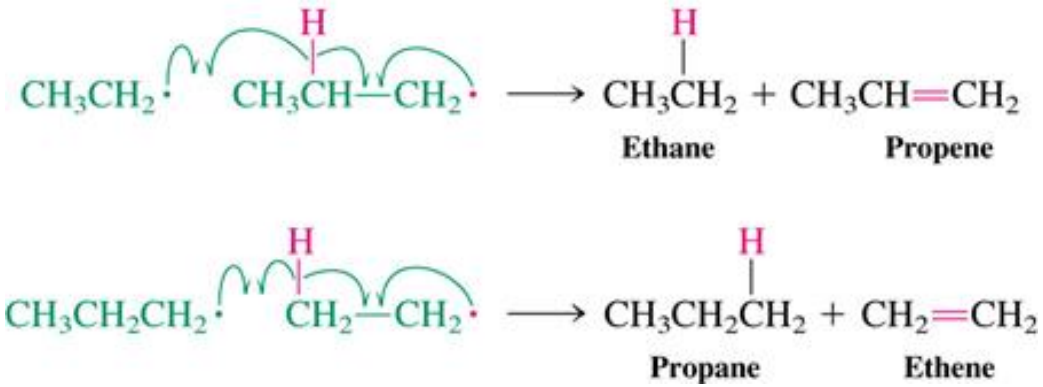
Homolytické štěpení



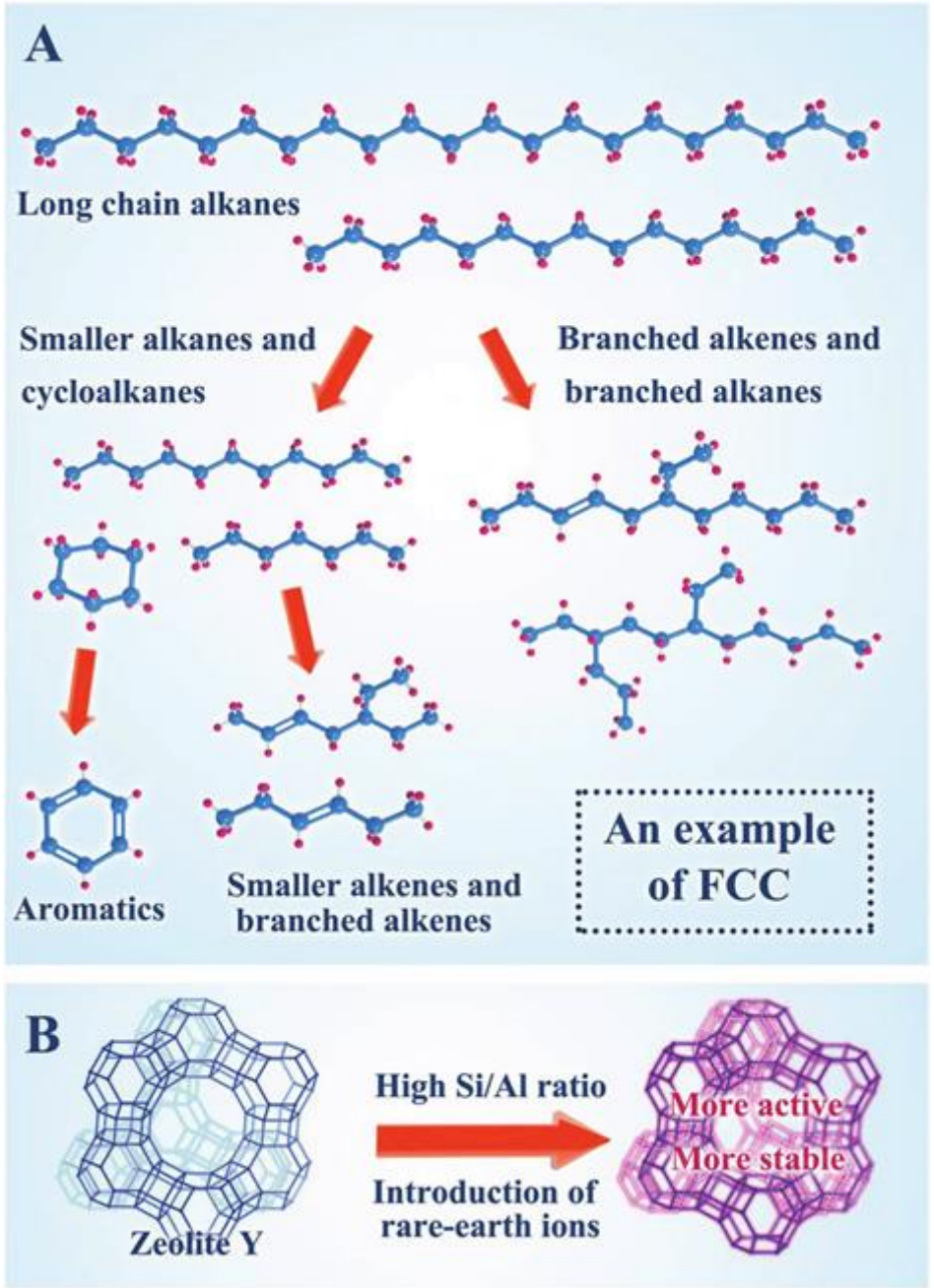
Rekombinace radikálů



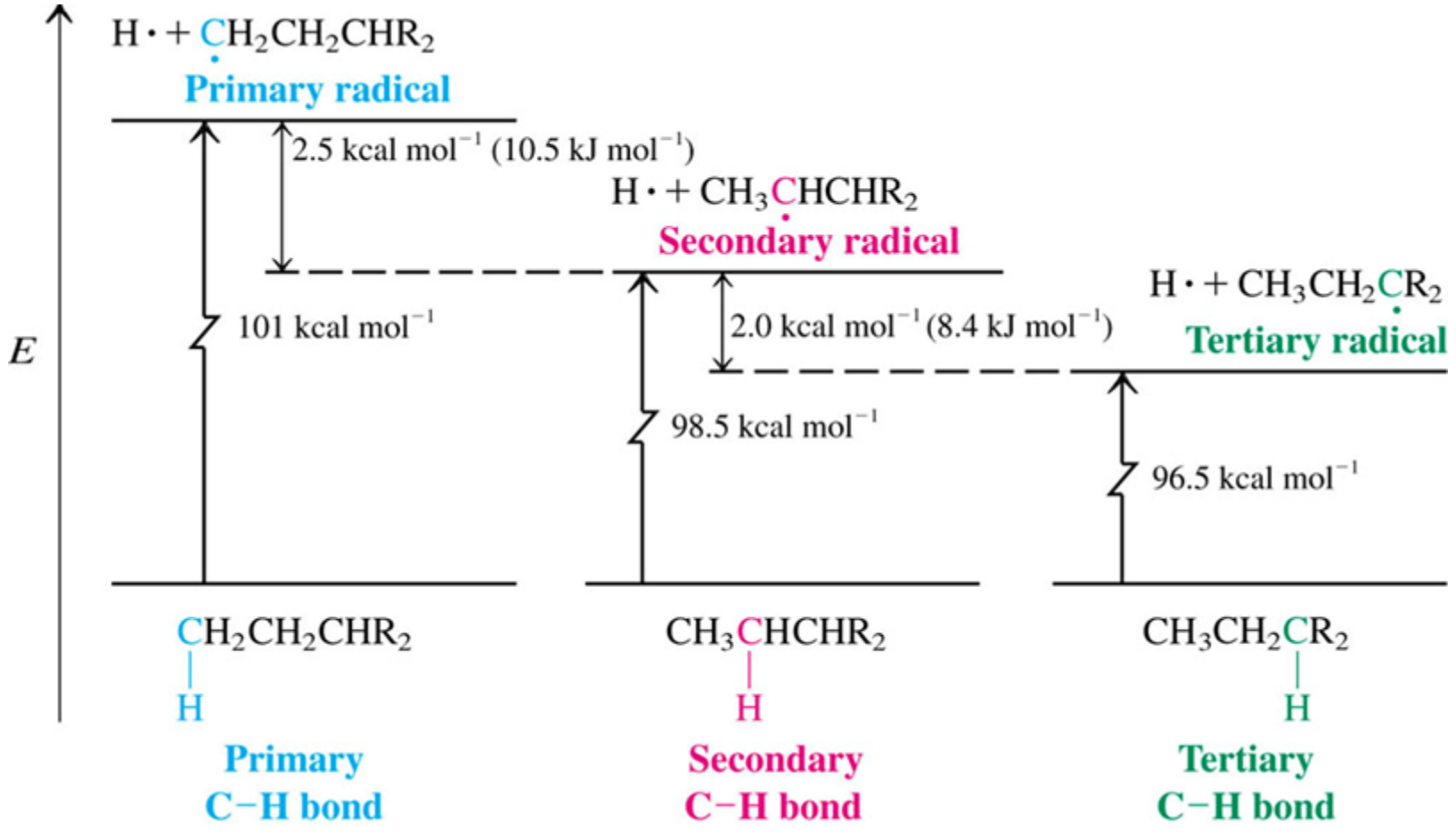
Abstrakce vodíku



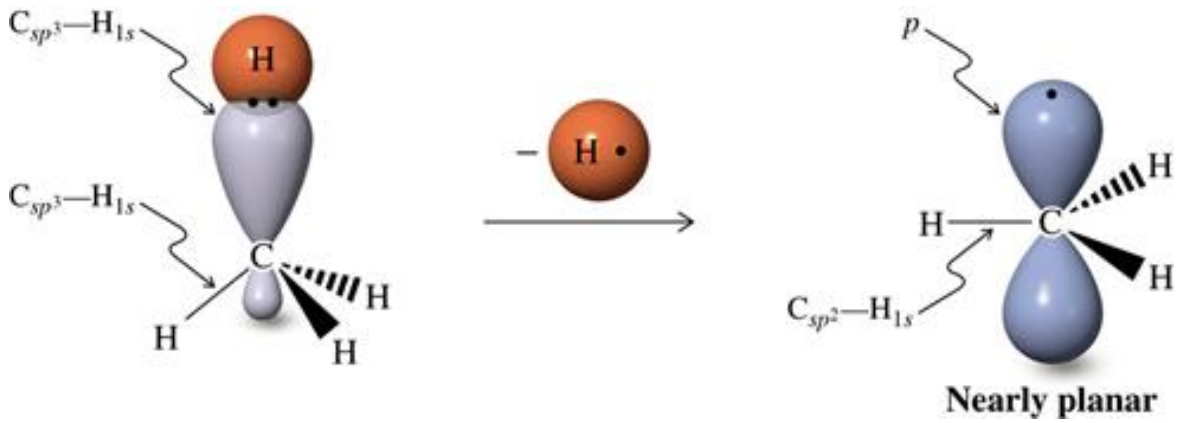
Fluidní Katalytické krakování



Uhlíkové radikály



Uhlíkové radikály



planární

hyperkonjugace

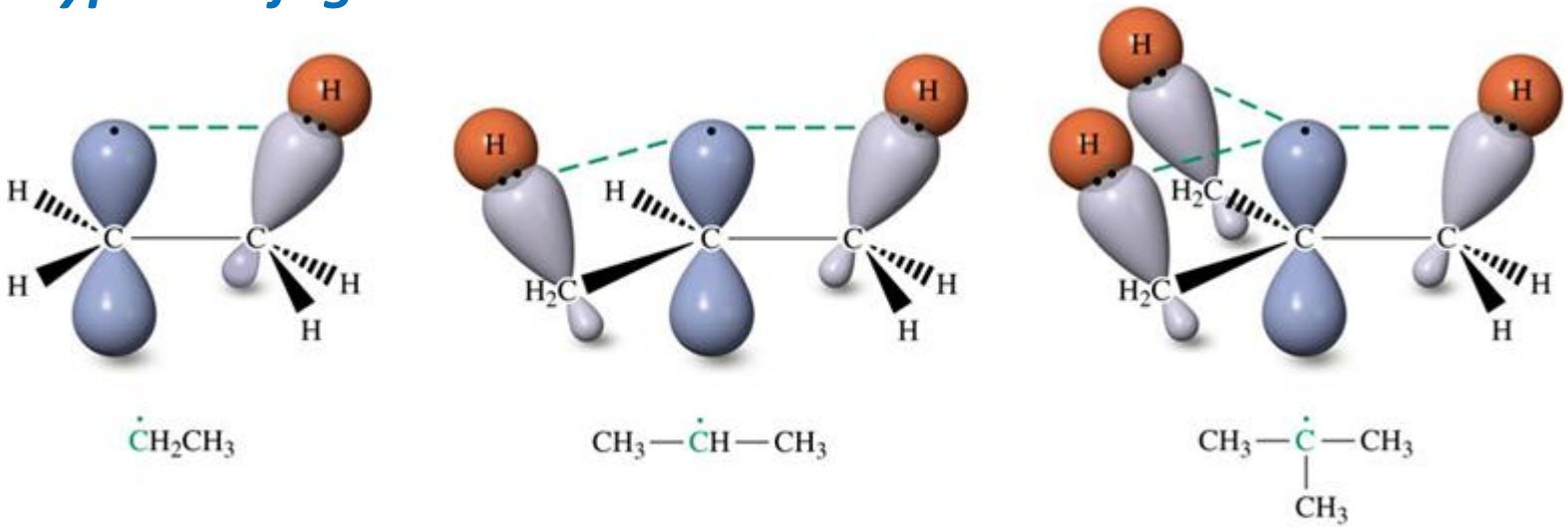


Table 3-2 Bond-Dissociation Energies for Some Alkanes

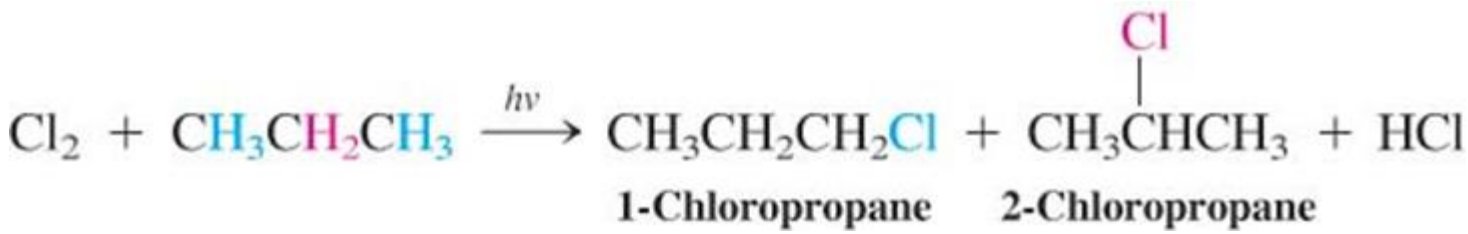
Compound	$DH°$ [kcal mol^{-1} (kJ mol^{-1})]	Compound	$DH°$ [kcal mol^{-1} (kJ mol^{-1})]
CH_3-H	105 (439)	CH_3-CH_3	90 (377)
C_2H_5-H	101 (423)	$C_2H_5-CH_3$	89 (372)
C_3H_7-H	101 (423)	$C_2H_5-C_2H_5$	88 (368)
$(CH_3)_2CHCH_2-H$	101 (423)	$(CH_3)_2CH-CH_3$	88 (368)
$(CH_3)_2CH-H$	98.5 (412)	$(CH_3)_3C-CH_3$	87 (364)
$(CH_3)_3C-H$	96.5 (404)	$(CH_3)_2CH-CH(CH_3)_2$	85.5 (358)
		$(CH_3)_3C-C(CH_3)_3$	78.5 (328)

Decreasing $DH°$

Decreasing $DH°$

Note: See footnote for Table 3-1.

Halogenace vyšších uhovodíků



43 % : 57 %

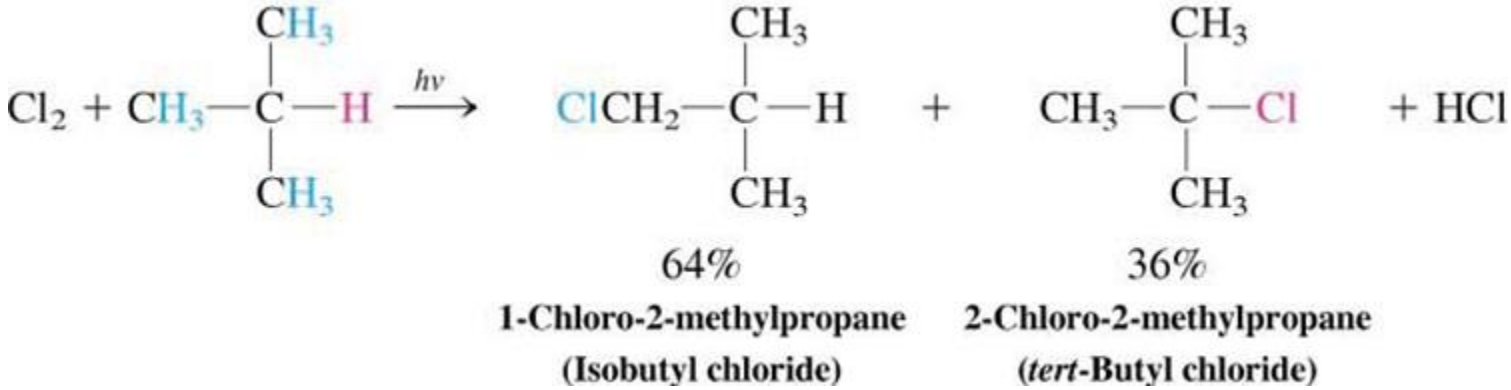
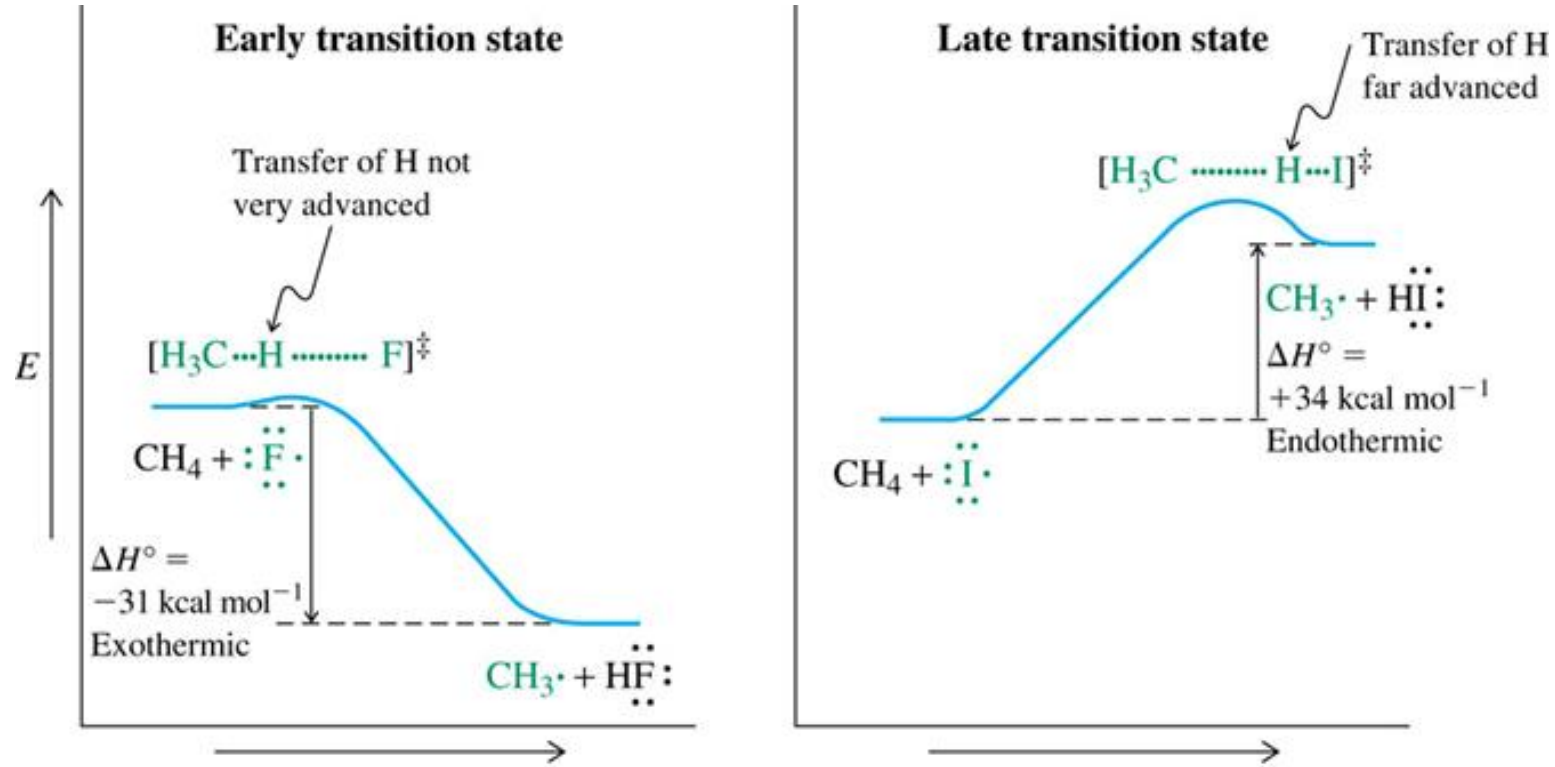
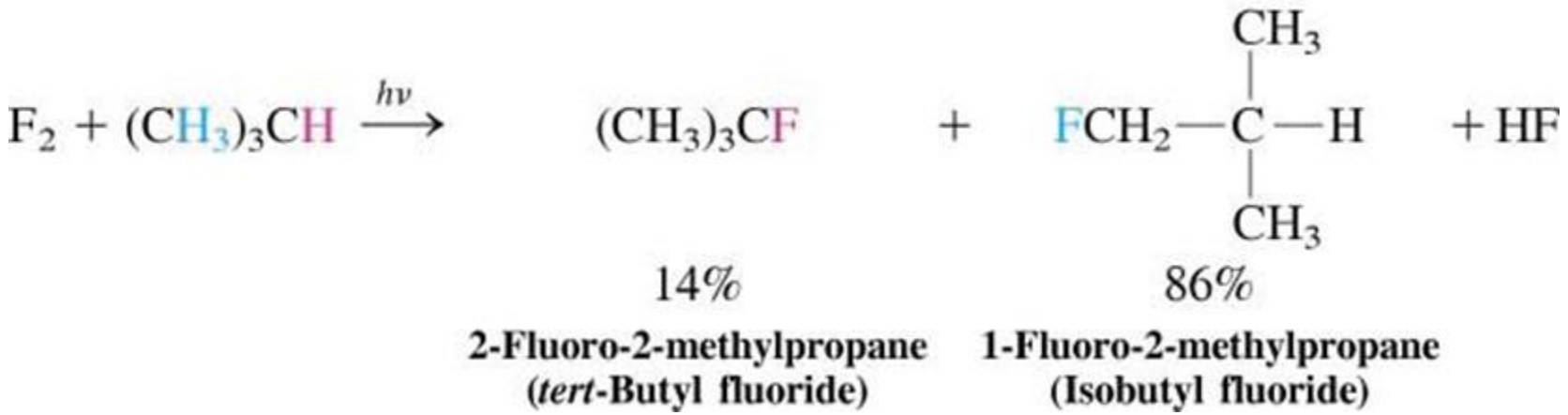


Table 3-5 Enthalpies of the Propagation Steps in the Halogenation of Methane [kcal mol^{-1} (kJ mol^{-1})]

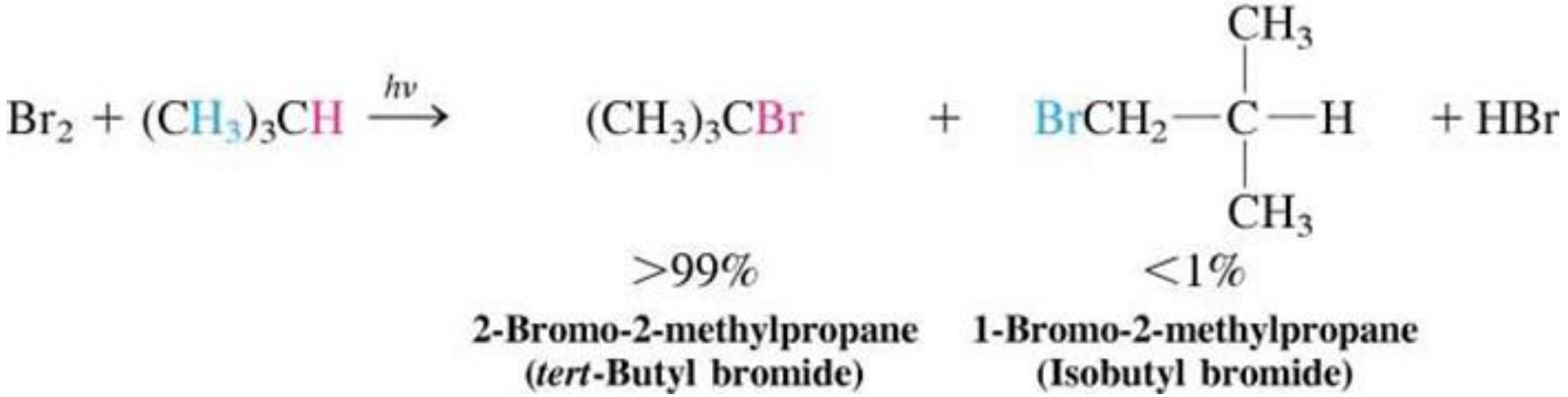
Reaction	F	Cl	Br	I
$:\ddot{X}\cdot + CH_4 \longrightarrow \cdot CH_3 + H\ddot{X}:$	−31 (−130)	+2 (+8)	+18 (+75)	+34 (+142)
$\cdot CH_3 + X_2 \longrightarrow CH_3\ddot{X}: + :\ddot{X}\cdot$	−72 (−301)	−27 (−113)	−24 (−100)	−21 (−88)
$CH_4 + X_2 \longrightarrow CH_3\ddot{X}: + H\ddot{X}:$	−103 (−431)	−25 (−105)	−6 (−25)	+13 (+54)



Fluorace 2-methylpropanu

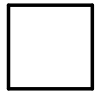


Bromination of 2-Methylpropane

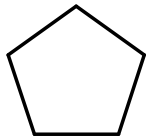


Cykloalkany

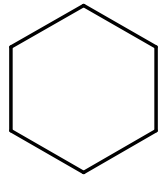
cyklopropan
b.v. -37.7°C



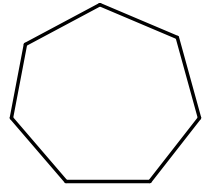
cyklobutan
b.v. 12°C



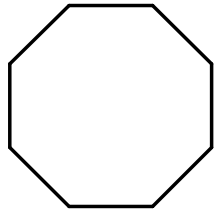
cyklopentan
b.v. 49.3°C



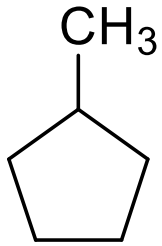
cyklohexan
b.v. 80.7°C



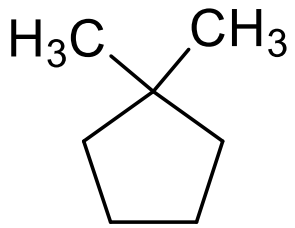
cykloheptan
b.v. 118.5°C



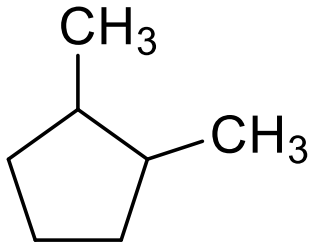
cyklooctan
b.v. 149°C



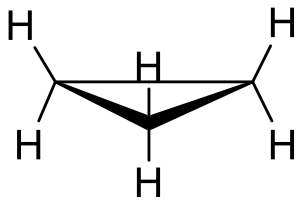
methylcyklopentan



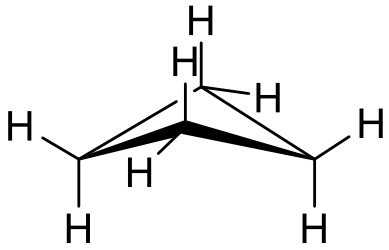
1,1-dimethylcyklopentan



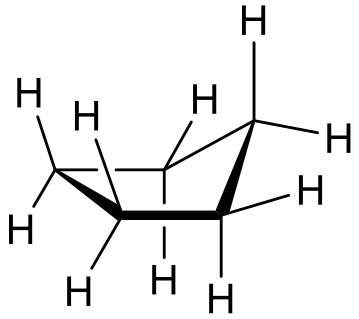
1,2-dimethylcyklopentan



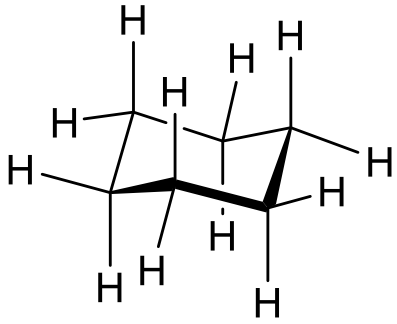
cyklopropan



cyklobutan



cyklopentan

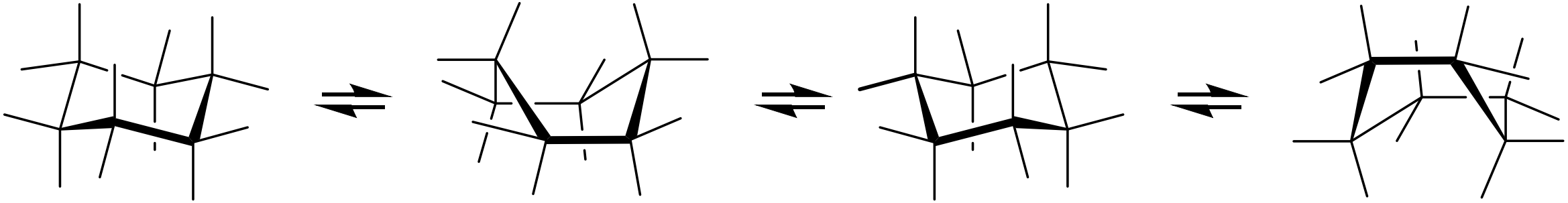


cyklohexan

Počet atomů uhlíku kruhu n	ΔH (kJ·mol^{-1})	ΔH/n (kJ·mol^{-1})	ΔH – n×659 (kJ·mol^{-1})
1 [a]	659	659	
2 [b]	1411	705	92
3	2093	697	115
4	2747	686	111
5	3322	664	27
6	3954	659	0
7	4639	662	26
8	5312	664	40

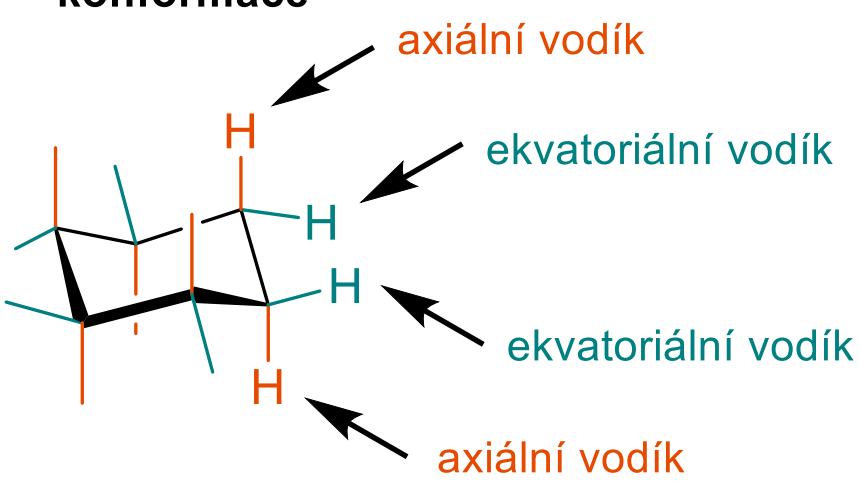
[a] (hodnota získaná ze spalných tepel alkanů. [b] Pro ethen jako nejmenší kruh.

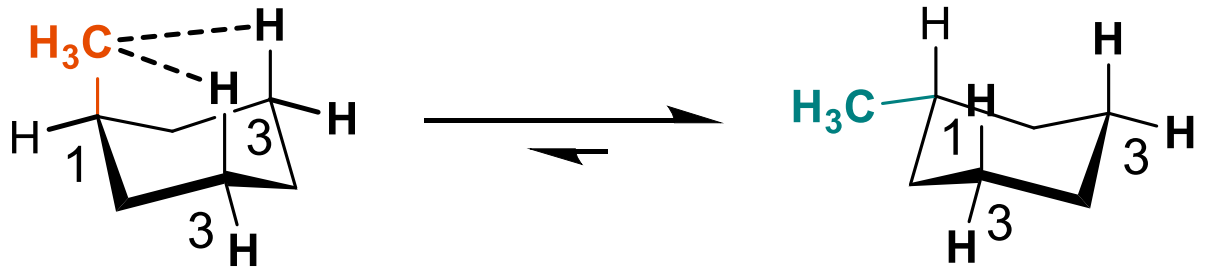
Konformace cyklohexanu



židličková konformace | **vaničková konformace** | **židličková konformace** | **vaničková konformace**

židličková konformace

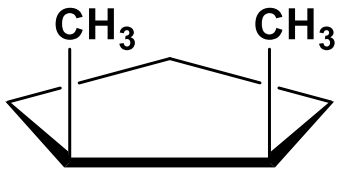




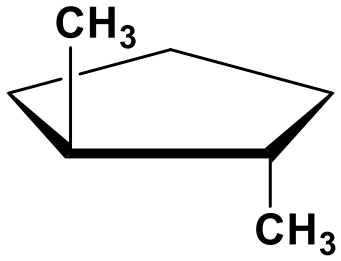
Me v axiálnípoloze
5%

Me ekvatoriální poloze
95%

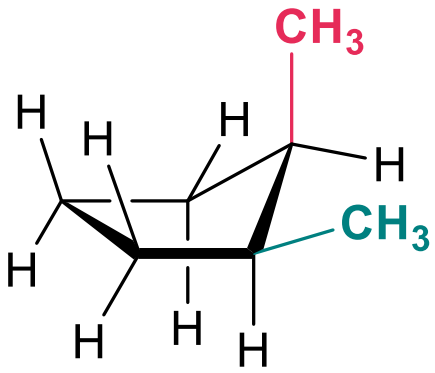
Cis a *trans* izomerie u cykloalkanů



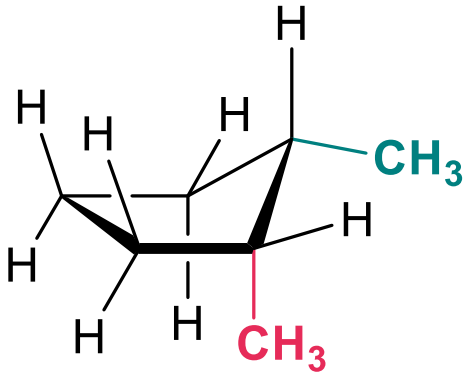
***cis*-1,2-dimethylcyklopentan**
t.v. 99°C



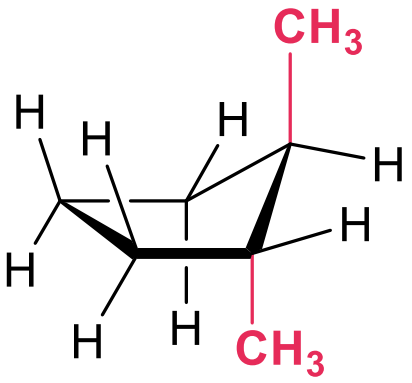
***trans*-1,2-dimethylcyklopentan**
t.v. 92°C



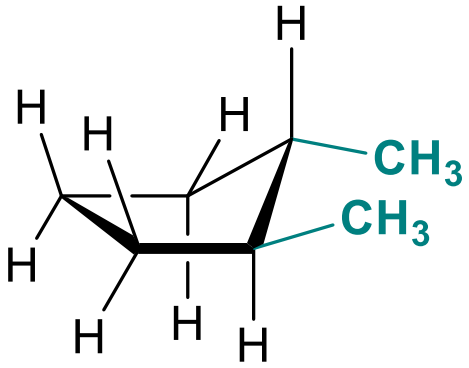
e,a



a,e

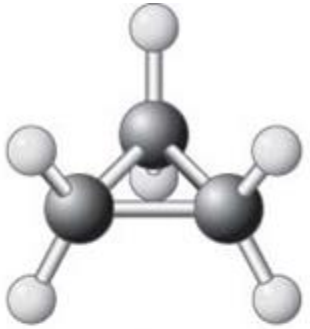


a,a

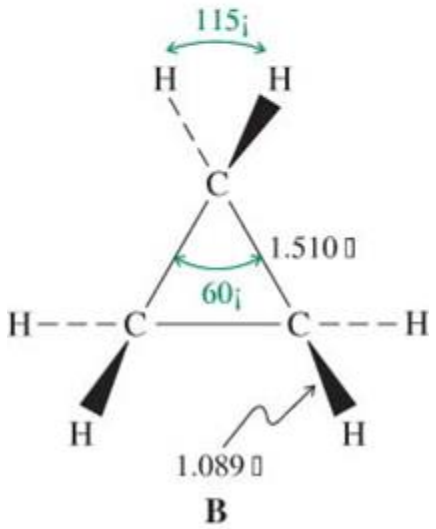


e,e
stabilnější

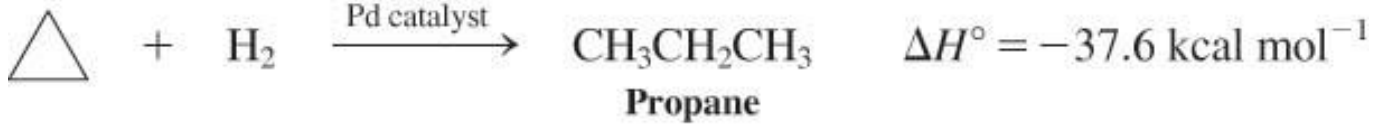
Cyklopropan



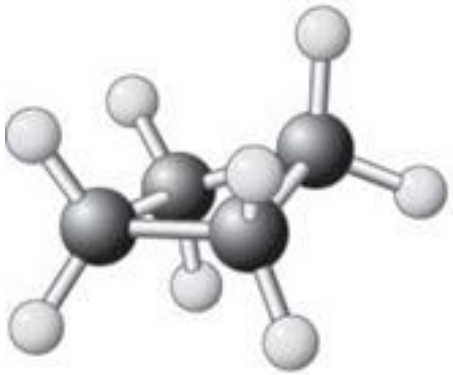
A



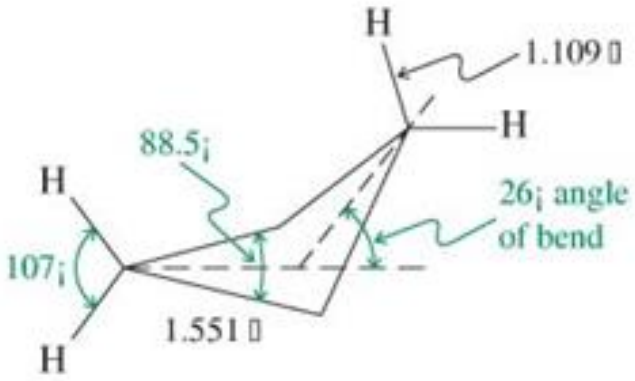
B



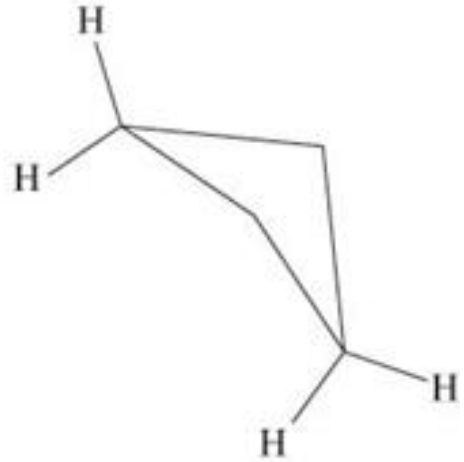
Cyklobutan



A



Rapid flip



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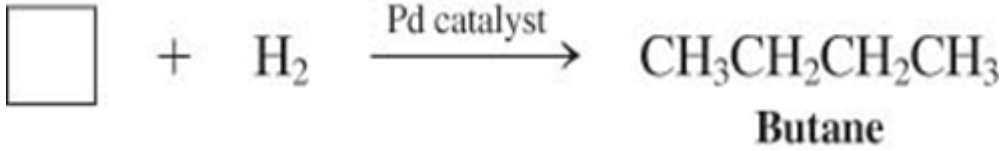
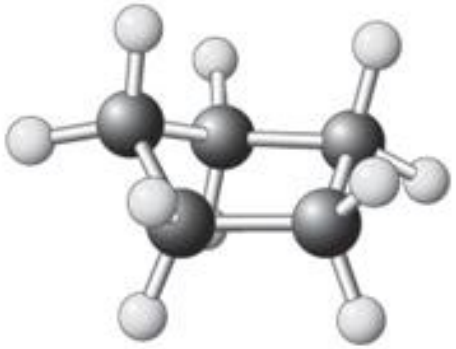
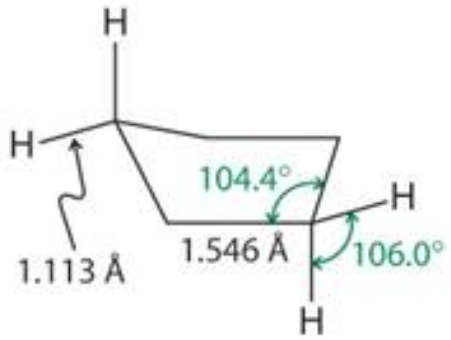


Butane

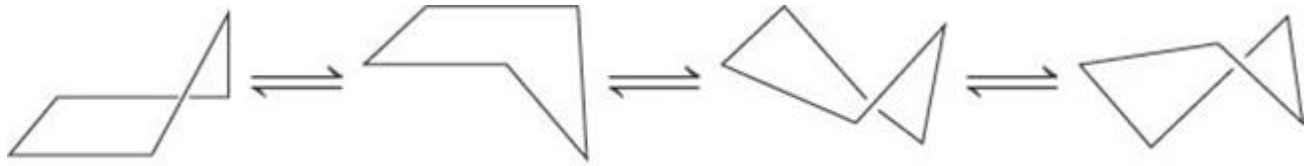
Cyklopentan



A



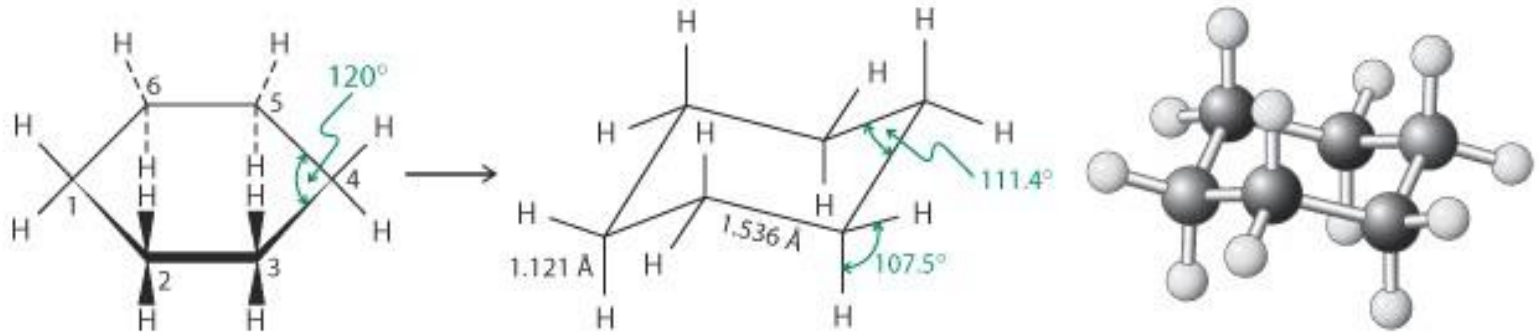
B



Envelope

Half chair

Cyklohexan



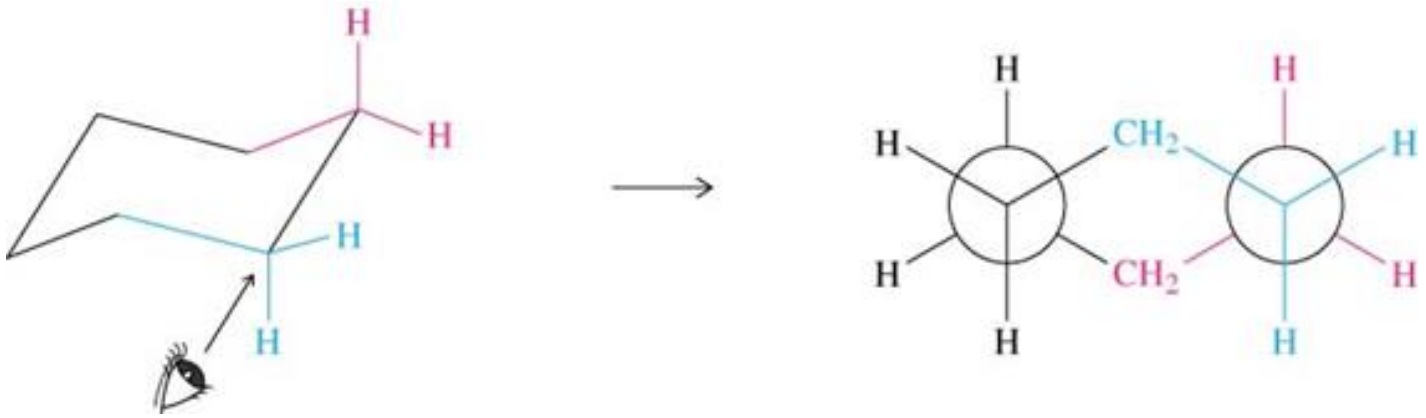
A

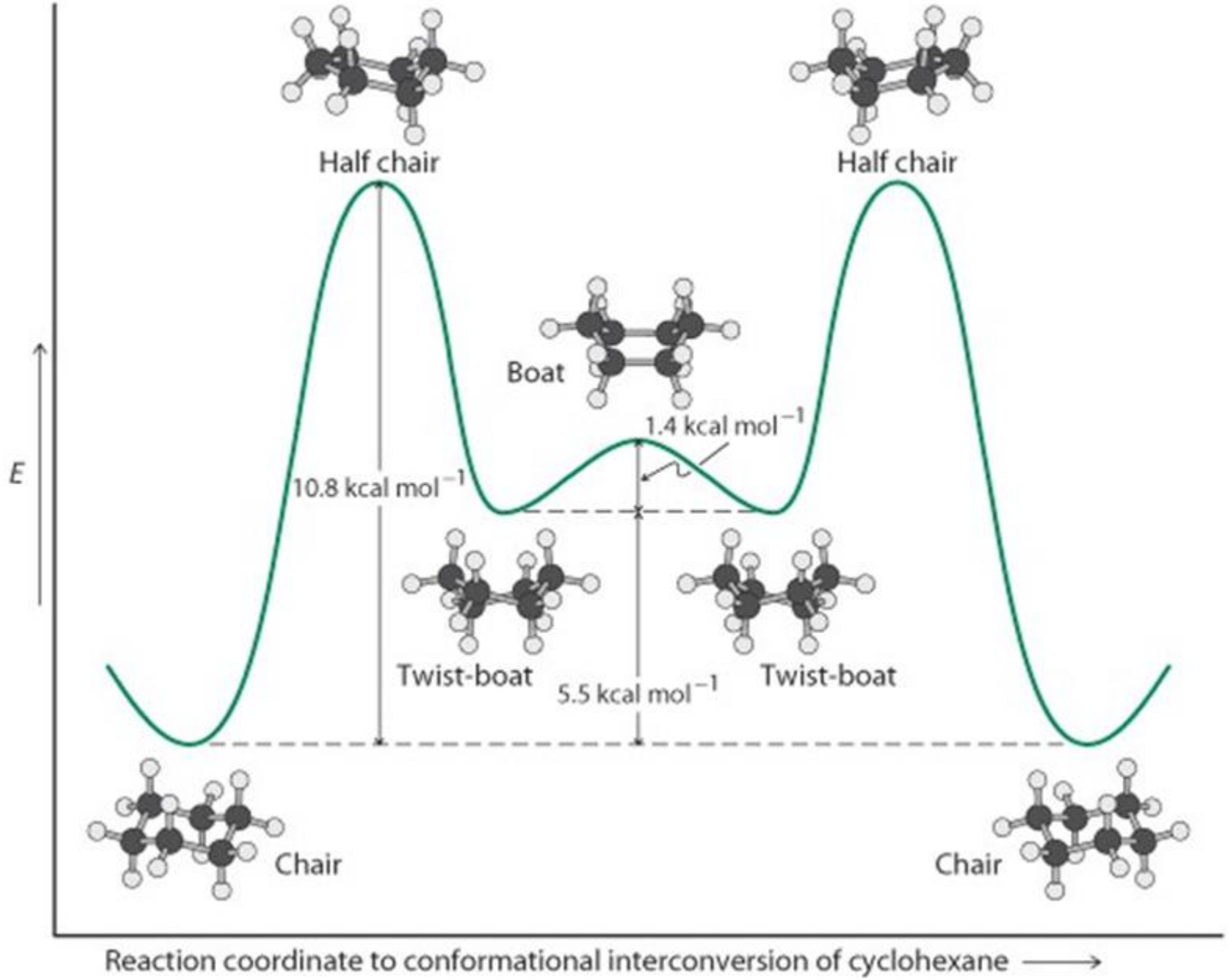
Planar cyclohexane
(120° bond angles;
12 eclipsing hydrogens)

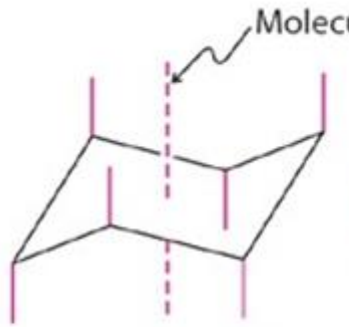
B

Chair cyclohexane
(Nearly tetrahedral bond angles;
no eclipsing hydrogens)

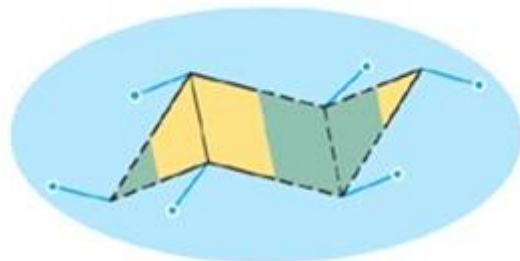
C



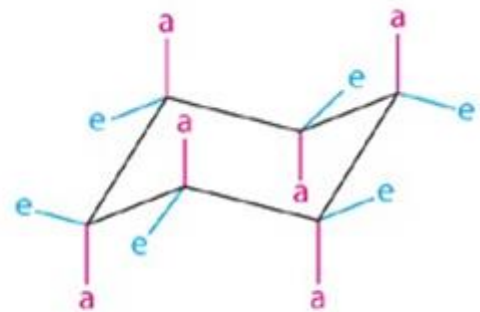

Half chair
Half chair
Boat
1.4 kcal mol^{-1}
10.8 kcal mol^{-1}
E
Twist-boat
Twist-boat
5.5 kcal mol^{-1}
Chair
Chair
Reaction coordinate to conformational interconversion of cyclohexane ⟶



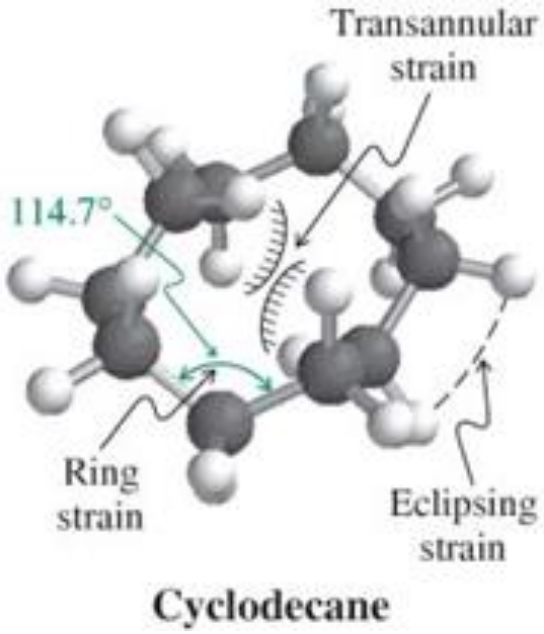
Axial positions



Equatorial positions

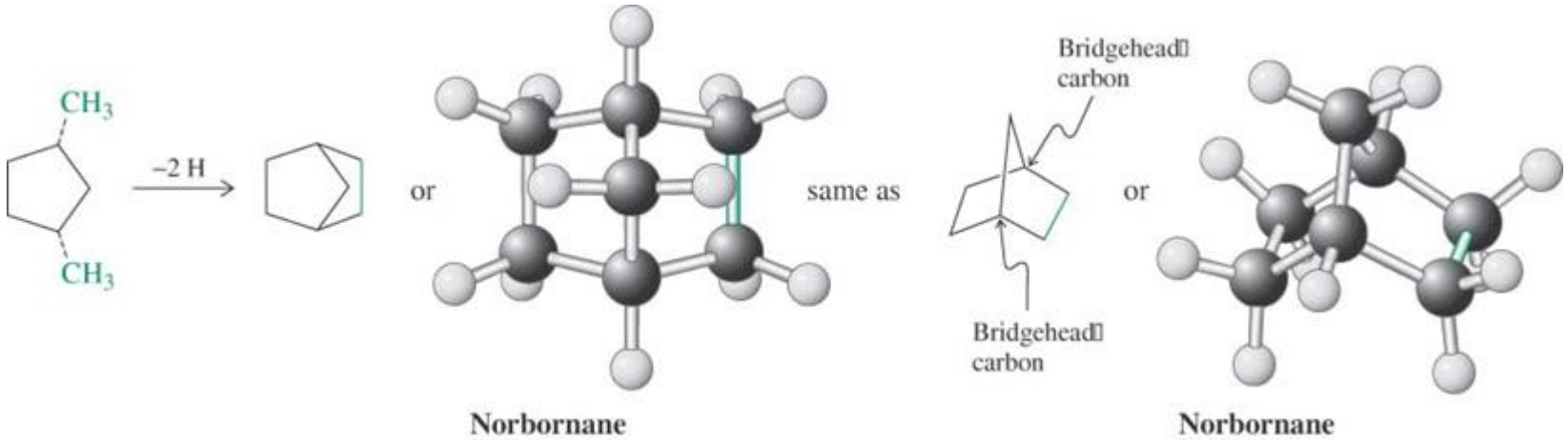


Axial (a) and equatorial (e) positions



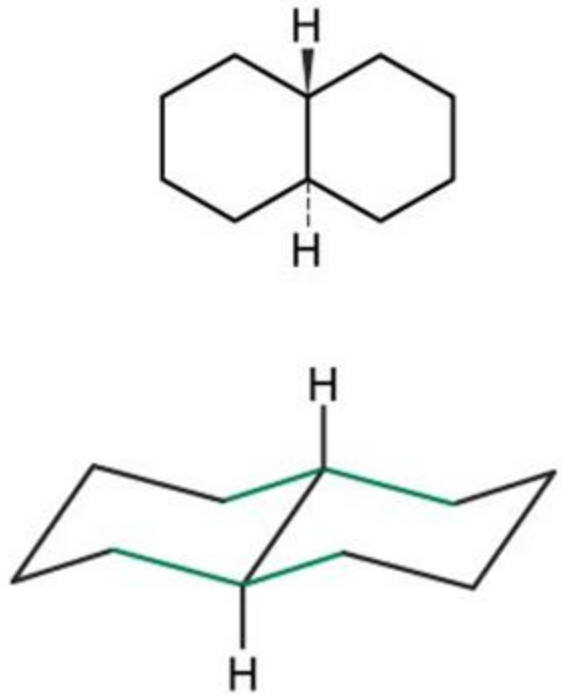
Cyclodecane

Strain energy of 14 kcal mol^{-1}.



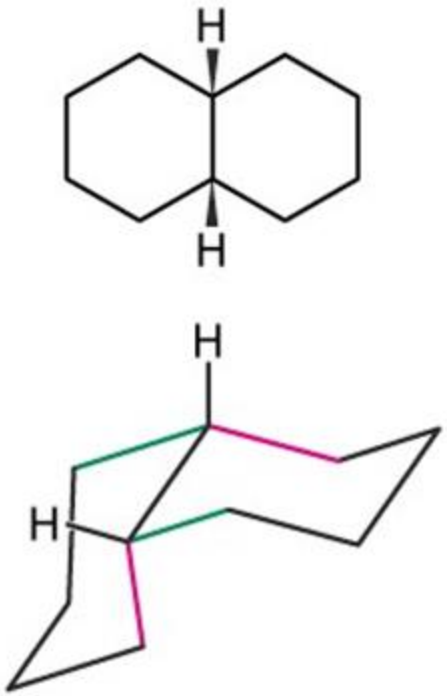
Norbornane

Norbornane



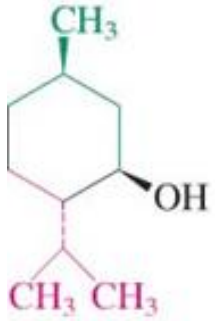
Equatorial C–C bonds

***trans*-Decalin**

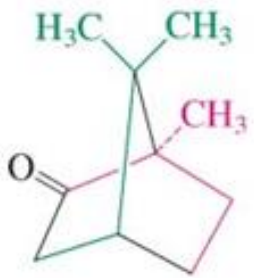


Axial C–C bonds Equatorial C–C bonds

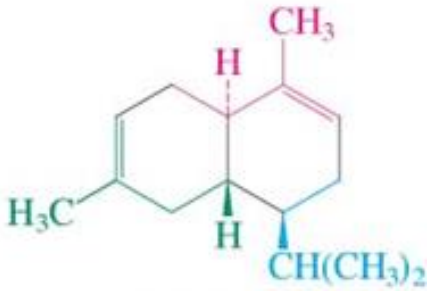
***cis*-Decalin**



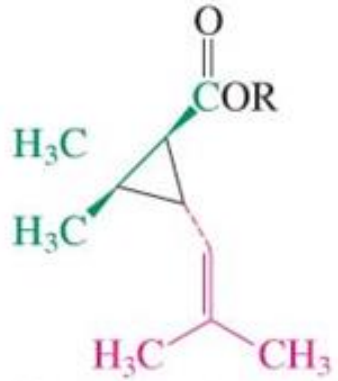
Menthol



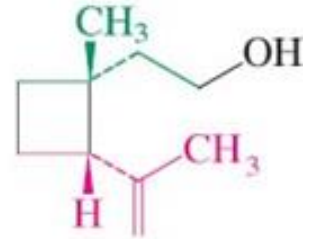
Camphor



β-Cadinene

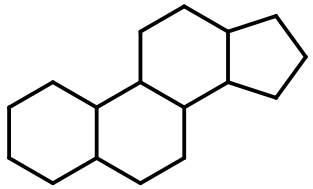


trans-Chrysanthemic acid (R = H)
trans-Chrysanthemic esters (R ≠ H)

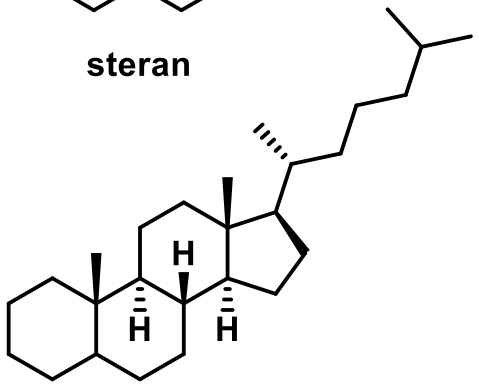


Grandisol

základní chemické skelety

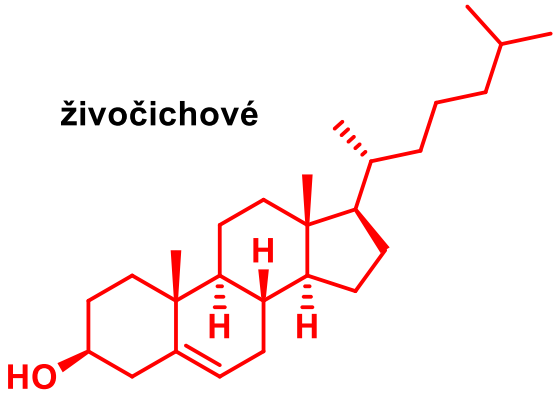


steran



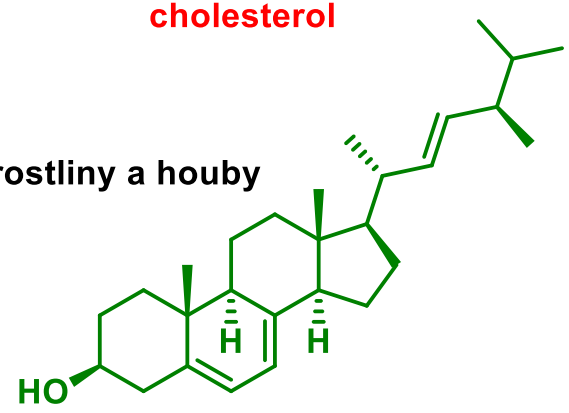
cholestan

živočichové



cholesterol

rostliny a houby



ergosterol