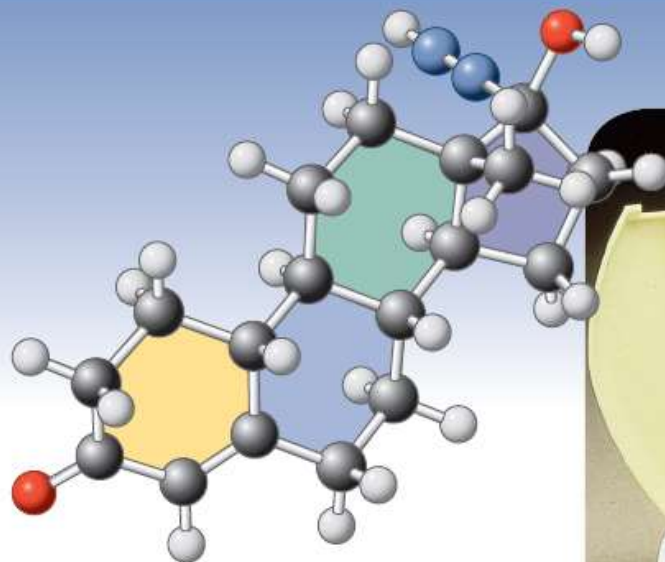


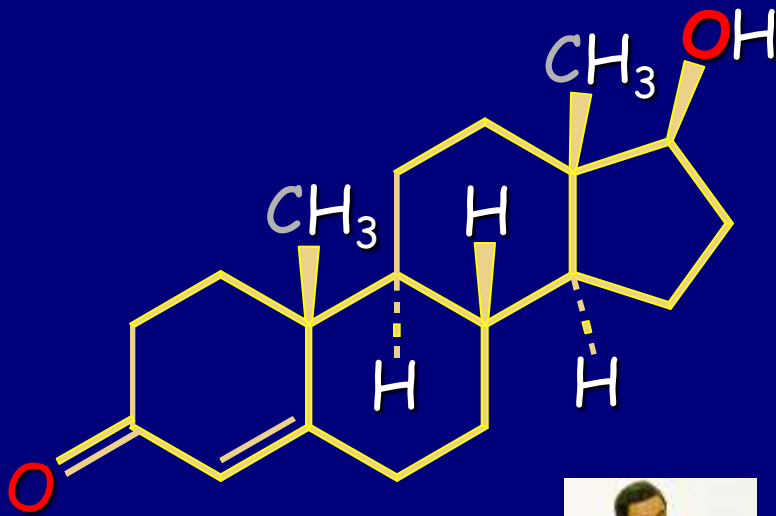
# Ciklični alkani



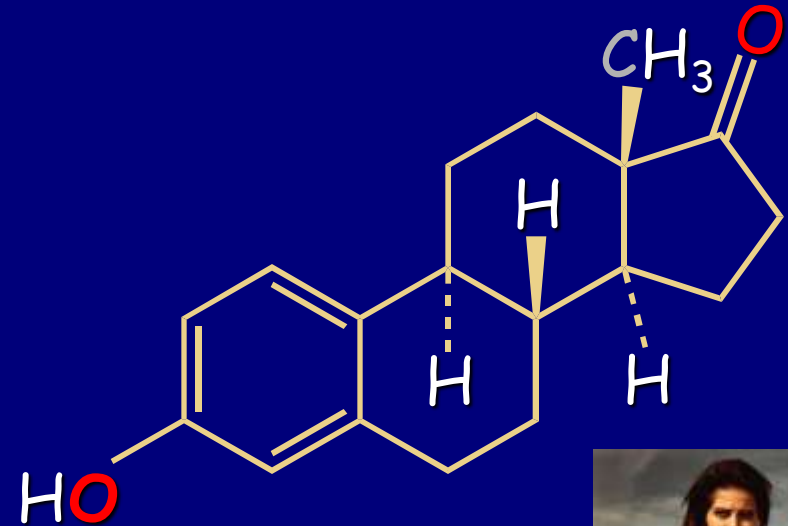
Skelet steroida koji čine policiklični alkani ilustrovan je noretindronom, jednim od glavnih sastojaka pilule za kontrolu začea.



# Steroidni hormoni



Testosteron



Estron



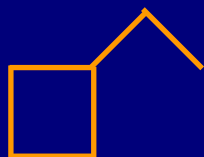
Polni hormoni regulišu razvoj i funkciju reproduktivnih organa;

# Cikloalkani $(CH_2)_n$ ne $C_nH_{2n+2}$

Rasprostranjenost u prirodi: "rigid scaffolding".

Imena: Cikloalkani  Ciklopropan, , , etc.

Supstituenti: Cikloalkil. Supstituisani cikloalkani: kod monosupstituisani, položaj supstituenat je "C1".

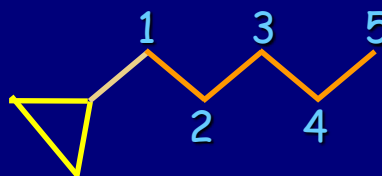


etilciklobutan (nije potrebno numerisanje)

Alkilcikloalkani ili cikloalkilalkani?

Manje jedinice se smatraju supstituentima većih!!!

IUPAC-novo pravilo:  
alkilcikloalkani

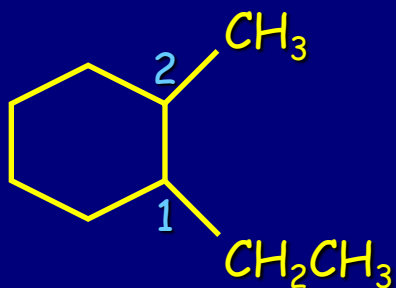


1-Ciklopropilpentan

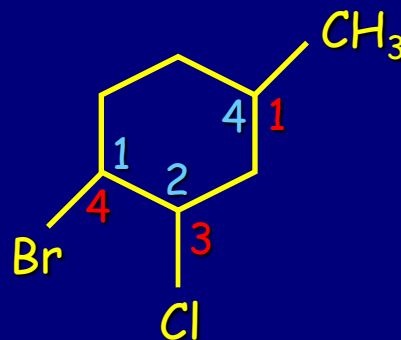
pentilciklopropan

# Disupstituisani:

- Najmanji brojevi za položaj supstituenata
- Redosled po abecedi



1-etil-2-metilcikloheksan



1,2,4 ne 1,3,4

1-bromo-2-hlor-4-metilcikloheksan

# Stereoizomeri

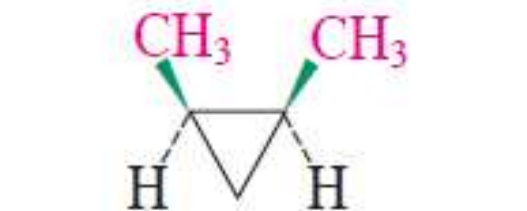
Cikloalkani imaju dve strane.

Sa dva i više supstituenata novi tip izomerije

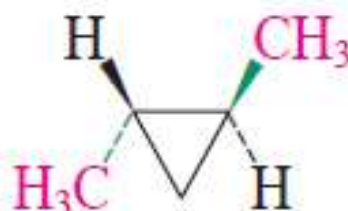
Supstituenti na istoj strani: **cis**

Supstituenti na suprotnim stranam: **trans**

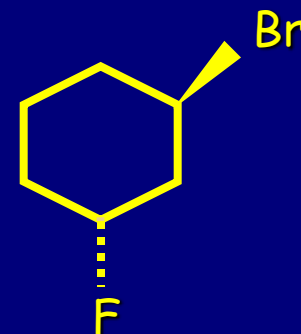
Stereoizomeri



*cis*-1,2-dimetilciklopropan



*trans*-1,2-dimetilciklopropan



*Trans*-1-brom-3-fluorcikloheksan

# Definicija stereoizomera:

Ista konektivnost (njihovi atomi vezani istim redosledom), ali se razlikuju u prostornom rasporedu

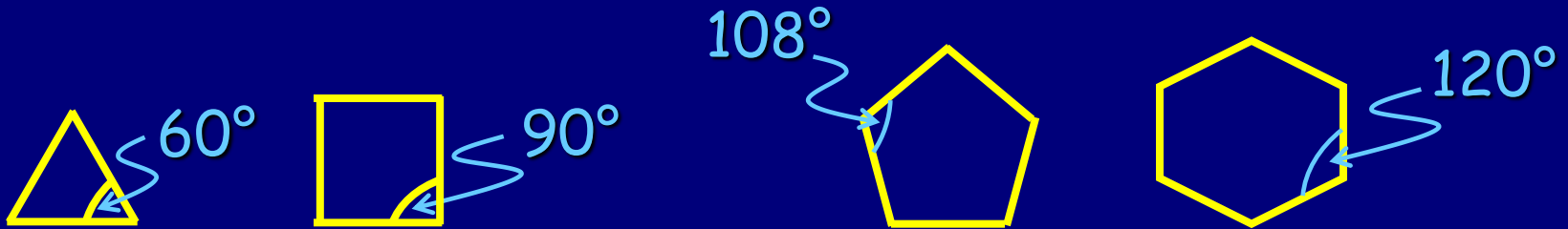
Ova definicija uključuje i rotamere (anti, gauche, itd.).

## Stereoizomer : rotamer

Stereoizomeri: su stabilni na sobnoj temperaturi, pretvaranje jednog u drugi moguće samo raskidanjem veza.

Rotameri: konformeri se brzo uravnotežuju rotacijom oko veza

# Napon prstena



$sp^3$ -ugljenik: uglovi veza  $109.5^\circ$

Kako možemo kvantifikovati "napon prstena"?

Potrebno je uporediti sa sistemom bez napona.

Toplota sagorevanja kao merilo stabilnosti.

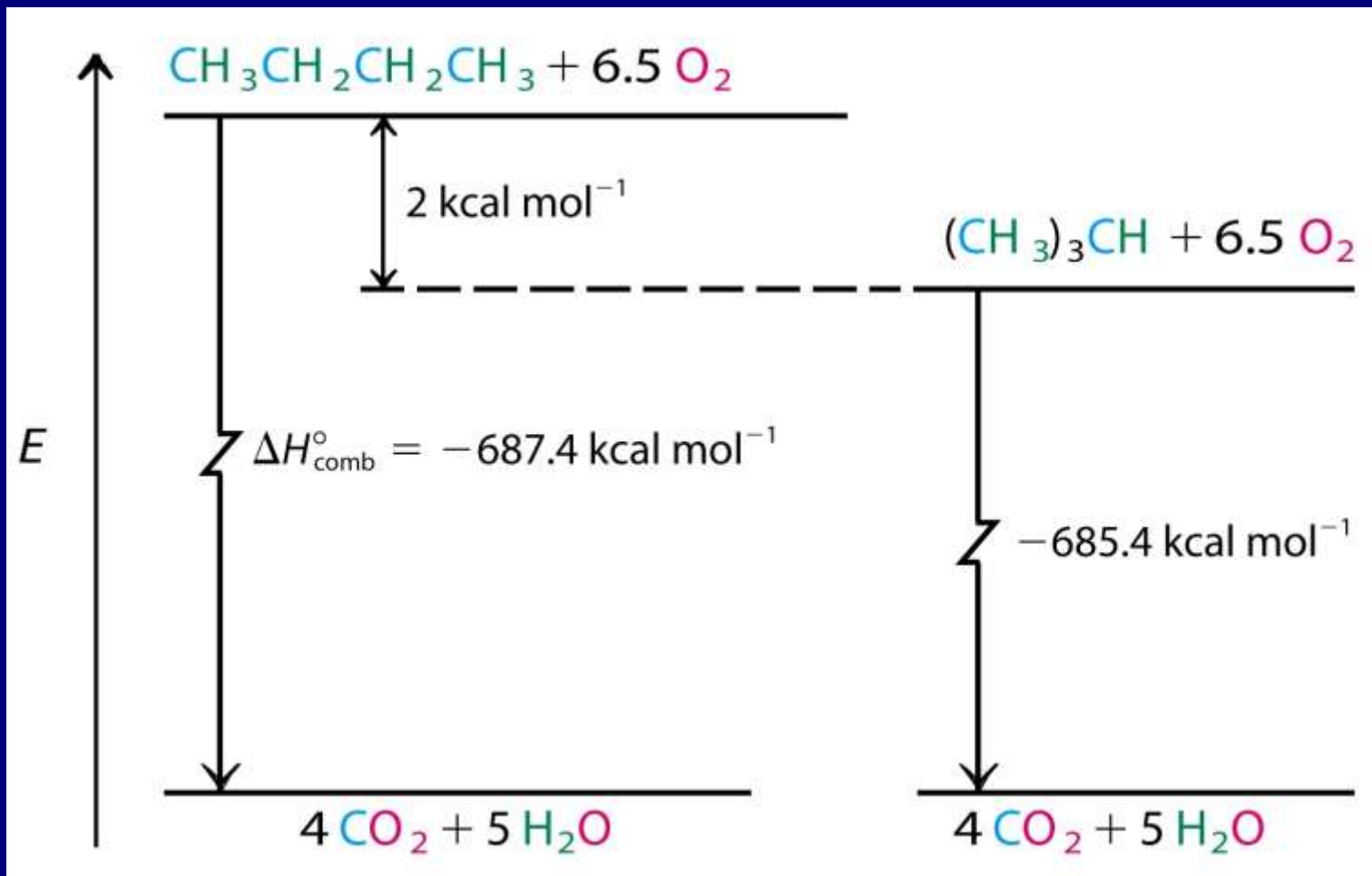
TABELA 3-7

Toplote sagorevanja ( $\text{kcal mol}^{-1}$ , normalizovane na  $25^\circ\text{C}$ )  
različnih organskih jedinjenja

Jedinjenje (stanje)	Ime	$\Delta H_{\text{sag}}^\circ$
$\text{CH}_4$ (gas)	metan	-212.8
$\text{C}_2\text{H}_6$ (gas)	etan	-372.8
$\text{CH}_3\text{CH}_2\text{CH}_3$ (gas)	propan	-530.6
$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$ (gas)	izomeri { butan	-687.4
$(\text{CH}_3)_3\text{CH}$ (gas)		
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ (gas)	pentan	-845.2
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ (tečan)	pentan	-838.8
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ (tečan)	heksan	-995.0
 (tečan)	cikloheksan	-936.9
$\text{CH}_3\text{CH}_2\text{OH}$ (gas)	etanol	-336.4
$\text{CH}_3\text{CH}_2\text{OH}$ (tečan)	etanol	-326.7
$\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (čvrst)	trščani šećer (saharoza)	-1348.2



# Primena: Relativni energetska sadržaj dva izomerna butana



Račvasti alkani su nešto stabilniji od izomera ravnog niza

Kod alkana za svaku dodatnu ( $\text{CH}_2$ ) grupu prirast od  $\delta\Delta H^\circ_{\text{sag}} \sim -157.4$ .

Na osnovu ovog je moguće predvideti  $\Delta H^\circ_{\text{sag}}$  (očekivano) za  $\text{C}_n\text{H}_{2n+2}$ :  $n \times 157.4$ .

Predviđanje kod cikloalkana :

$\Delta H^\circ_{\text{sag}}$  (očekivano)  $(\text{CH}_2)_n$ :  $n \times 157.4$ .

Razlika između očekivane i eksperimentalne vrednosti je napon prstena

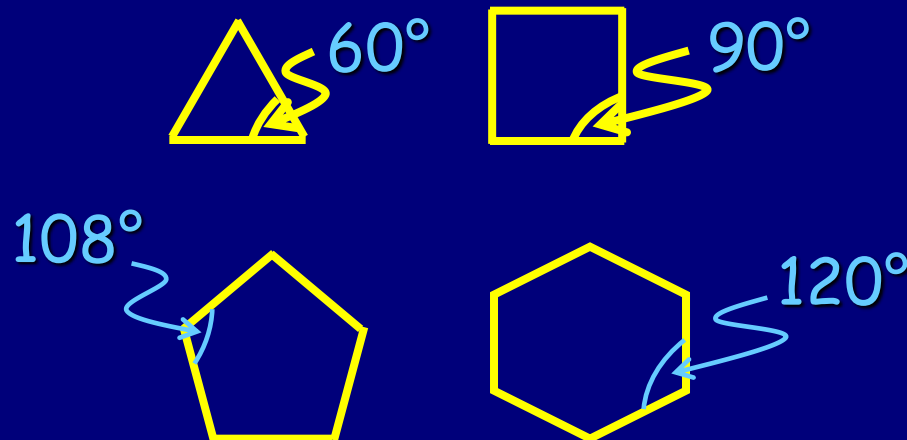
TABELA 4-2

Izračunate i eksperimentalne vrednosti toplote sagorevanja ( $\text{kcal mol}^{-1}$ ) različitih cikloalkana

Veličina prstena ( $C_n$ )	$\Delta H_{\text{sag}}^{\circ}$ (izračunato)	$\Delta H_{\text{sag}}^{\circ}$ (eksperimentalno)	Ukupan napon	Napon po $\text{CH}_2$ grupi
3	-472.2	-499.8	27.6	9.2
4	-629.6	-655.9	26.3	6.6
5	-787.0	-793.5	6.5	1.3
6	-944.4	-944.5	0.1	0.0
7	-1101.8	-1108.2	6.4	0.9
8	-1259.2	-1269.2	10.0	1.3
9	-1416.6	-1429.5	12.9	1.4
10	-1574.0	-1586.0	14.0	1.4
11	-1731.4	-1742.4	11.0	1.1
12	-1888.8	-1891.2	2.4	0.2
14	-2203.6	-2203.6	0.0	0.0

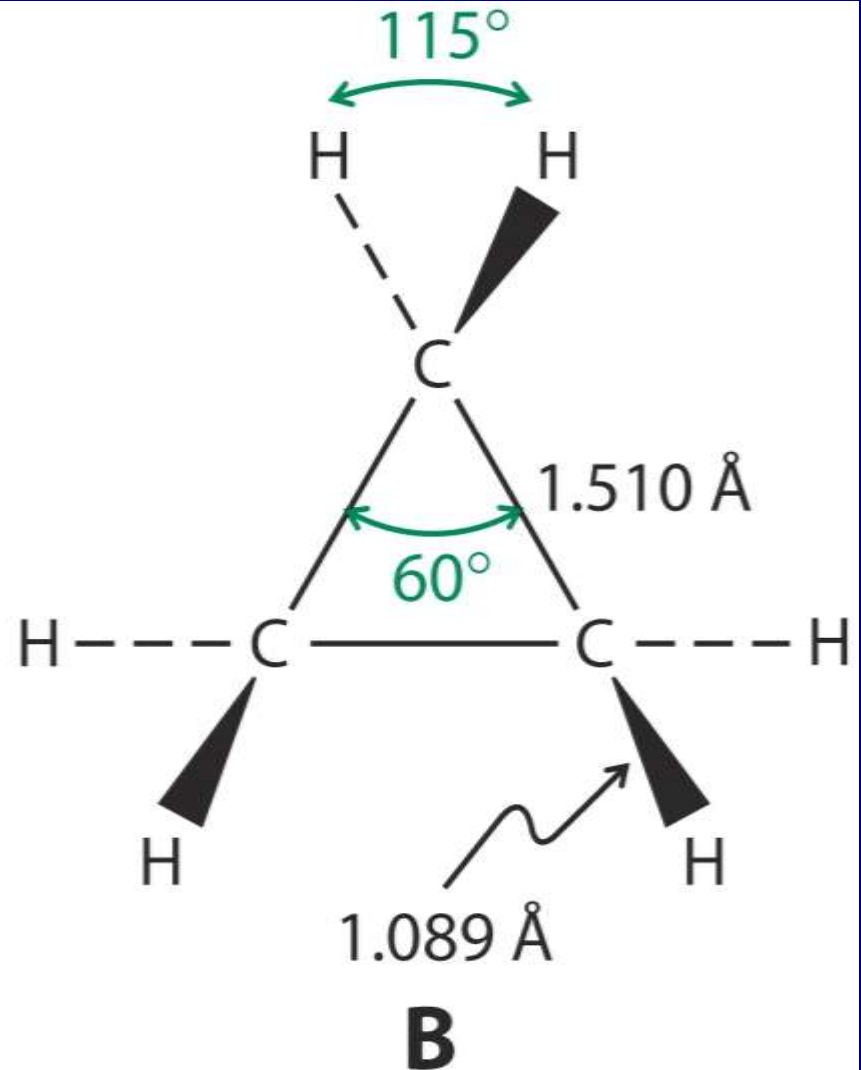
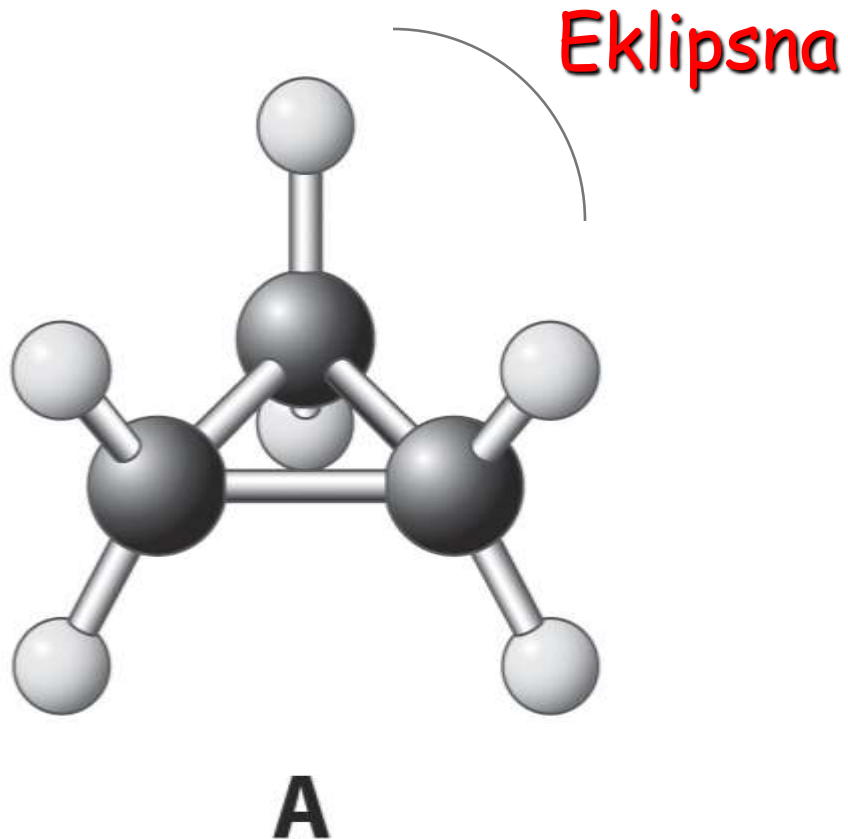
Napomena: izračunati brojevi su zasnovani na vrednosti  $-157,4 \text{ kcal mol}^{-1}$  za  $\text{CH}_2$  grupu

Mali prstenovi (3, 4)  
 Obični prstenovi (5, 6, 7)  
 Srednji prstenovi (8-12)  
 Veliki prstenovi (>12)

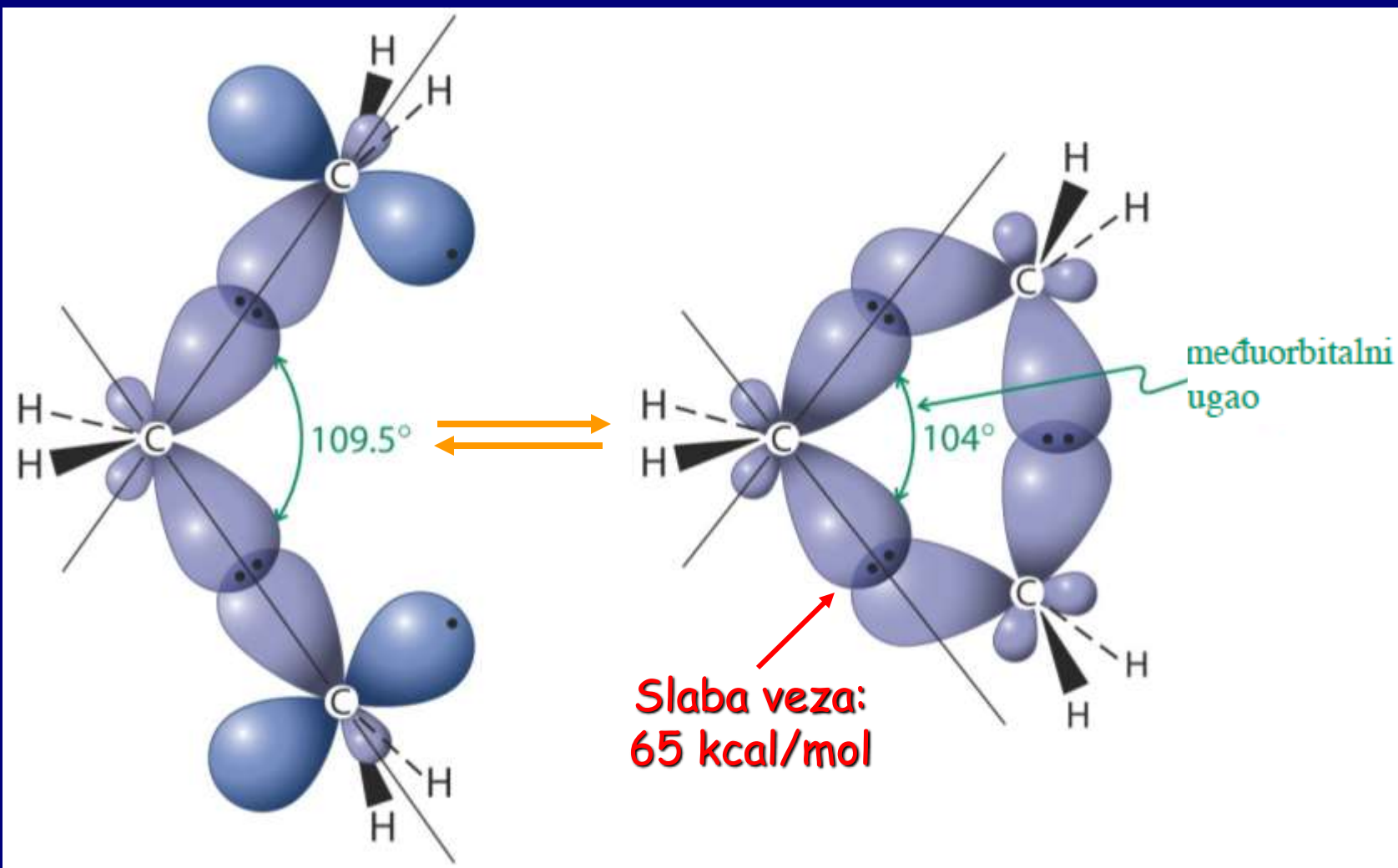


- Napon prstena:**
1. Uglovi veza  
(posebno C3 i C4)
  2. Eklipsnost
  3. Transanularne  
interakcije (posebno  
kod srednjih prstenova)

# Ciklopropan

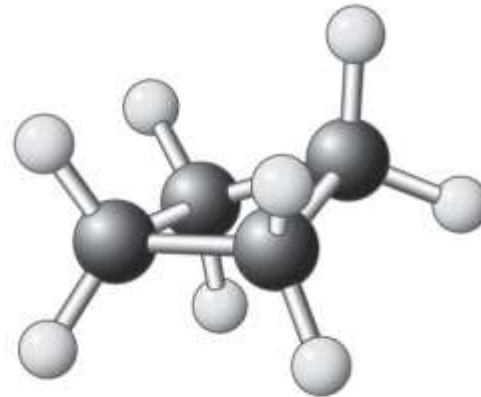


# Savijene veze kod ciklopropana

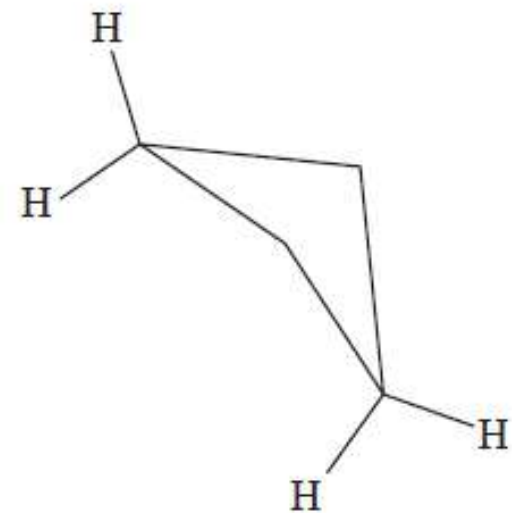
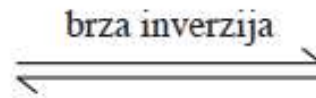
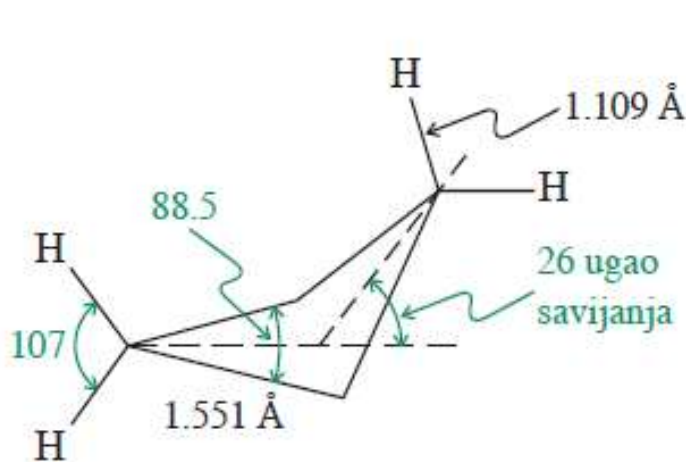


Trimetilen diradikal

# Ciklobutan: "nabiranje" se smanjuje eklipsnost

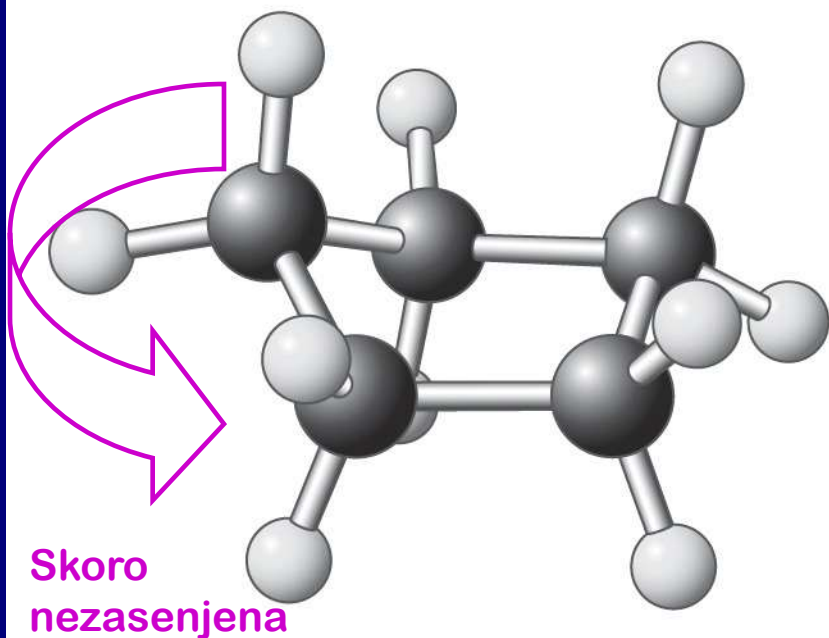


A

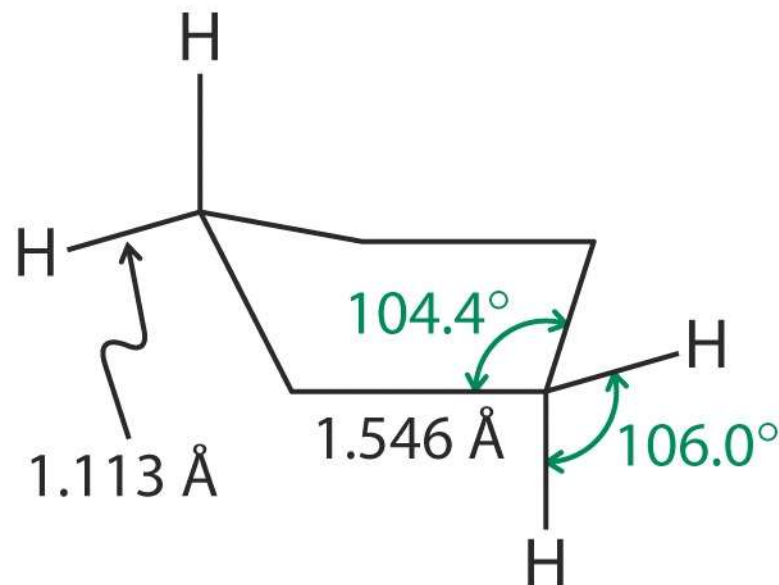


B

# Ciklopentantan: konformacija koverte



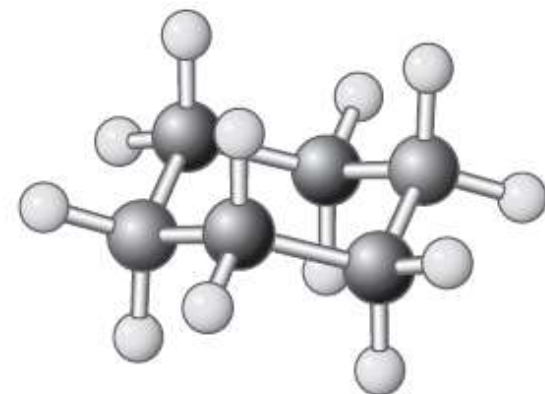
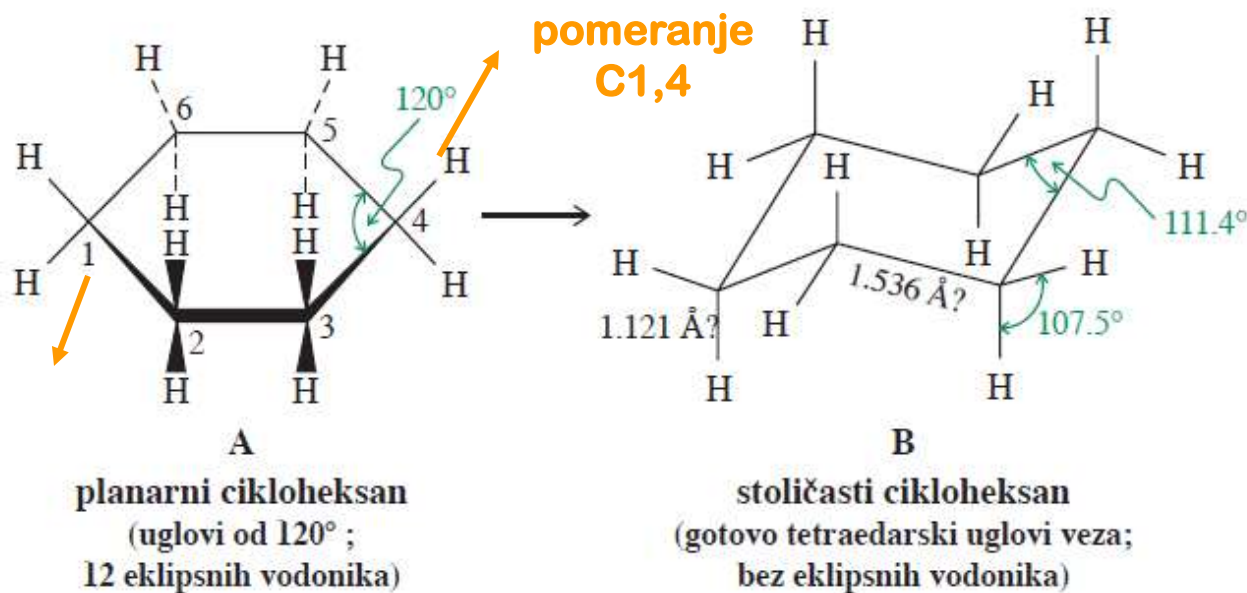
**A**



**B**

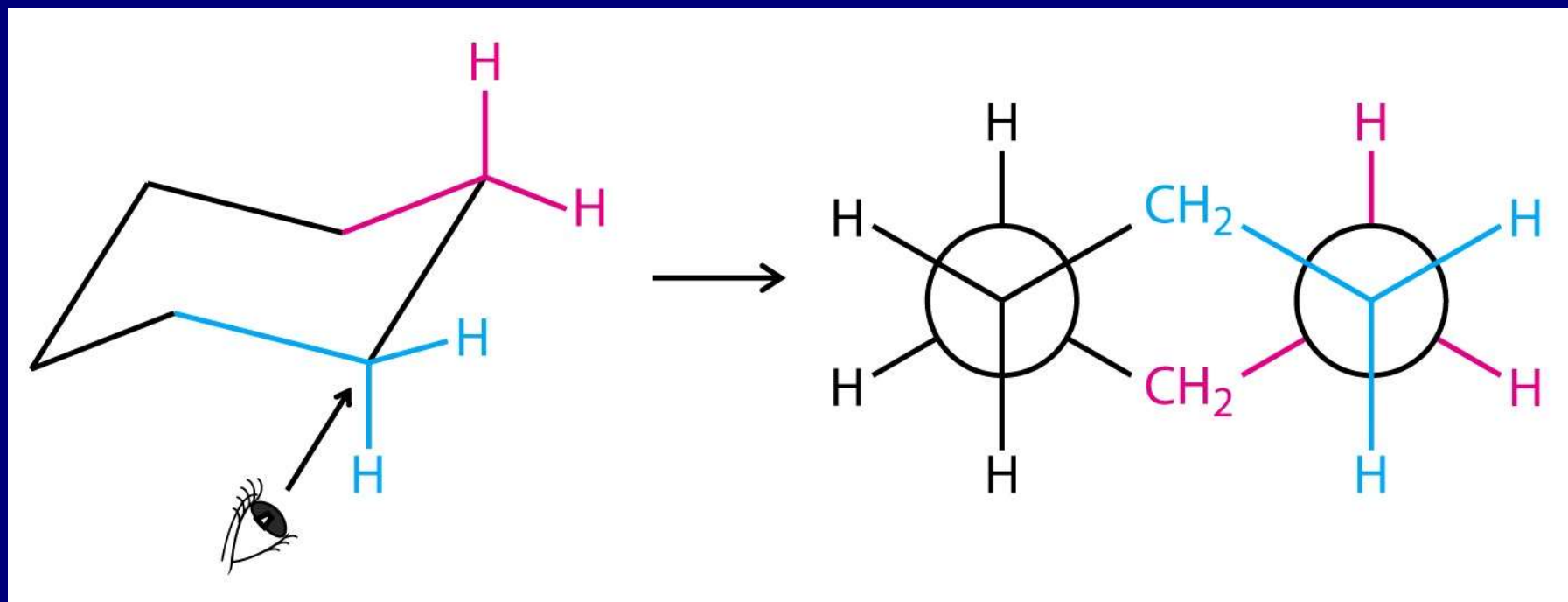


# Cikloheksan: cikloalkan bez napona; konformacija stolice

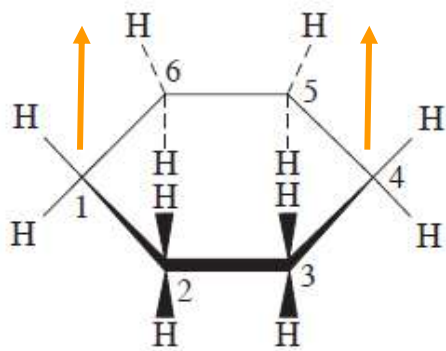


Veoma slične vrednosti za izračunatu i eksperimentalno određenu toplotu sagorevanja:  $-944,4 : -944,5 \text{ kcal mol}^{-1}$

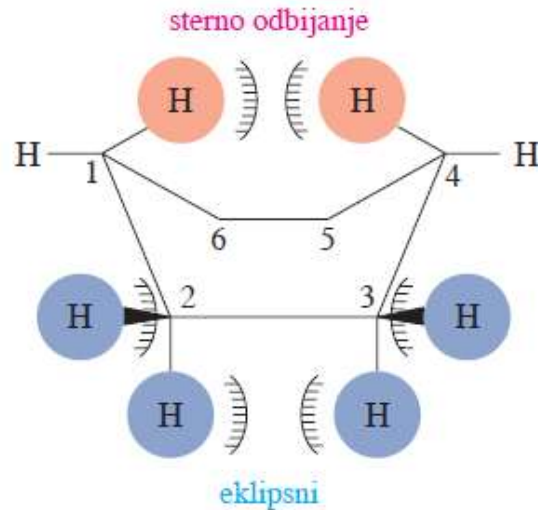
# Newman-ova projekcija cikloheksana-nezasenjena



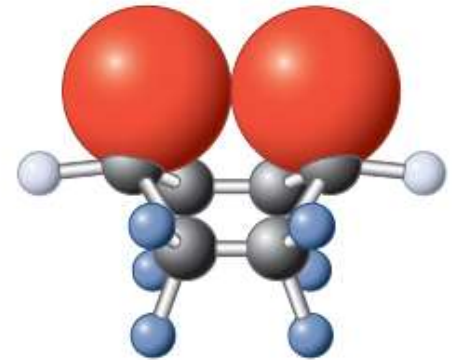
# Konformacija lađe, manje stabilna zbog eklipsnih interakcija i transanularnog napona



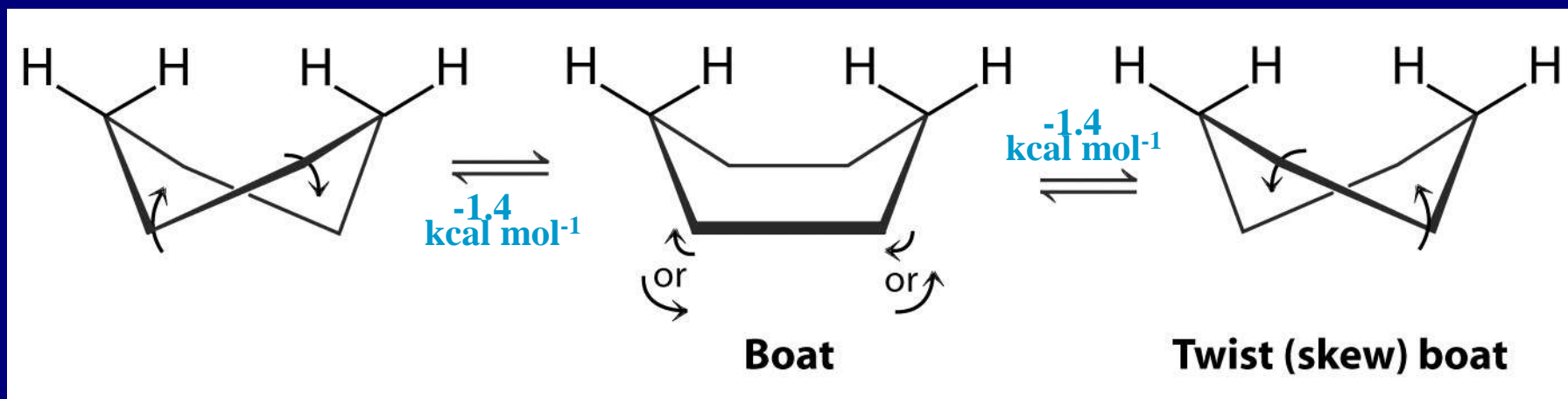
planarni cikloheksan



oblik lađe cikloheksana

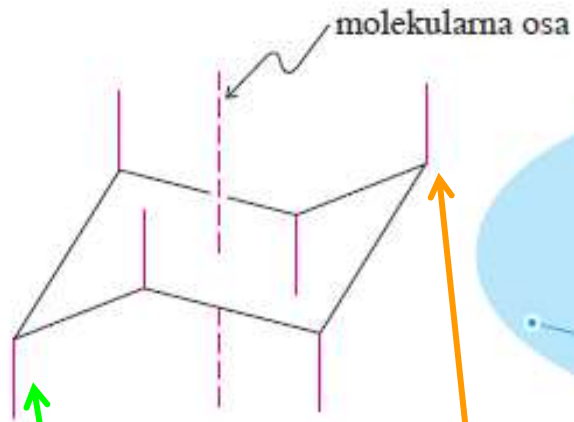


# ...zato se lađa uvija.



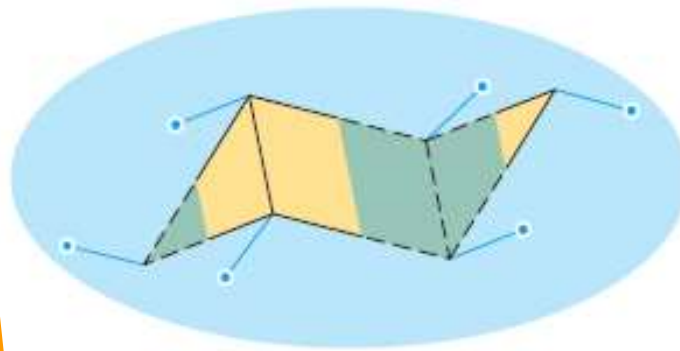
Dva moguća oblika uvijene lađe se međusobno izmenjuju preko konformera lađe kao prelaznog stanja

# Kako nacrtati cikloheksan u konformaciji stolice

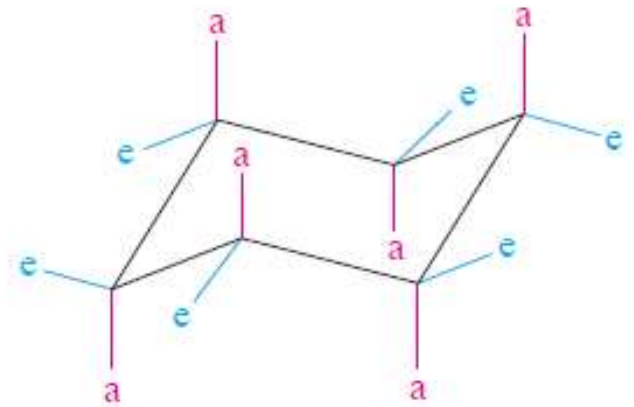


"dole"

"gore"

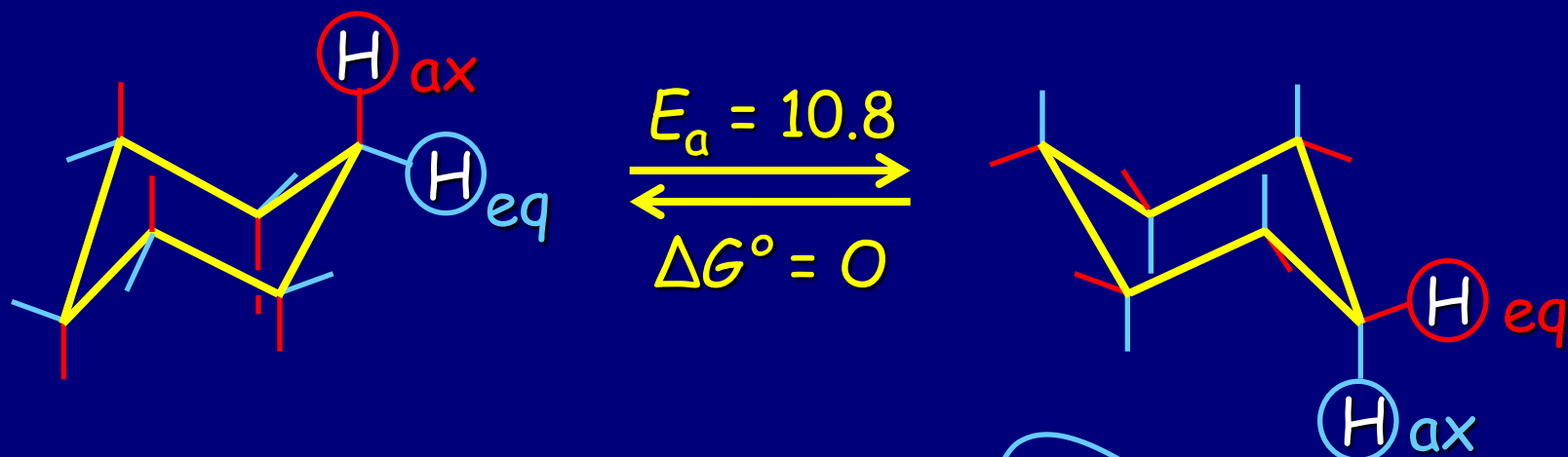


ekvatorijalni položaj



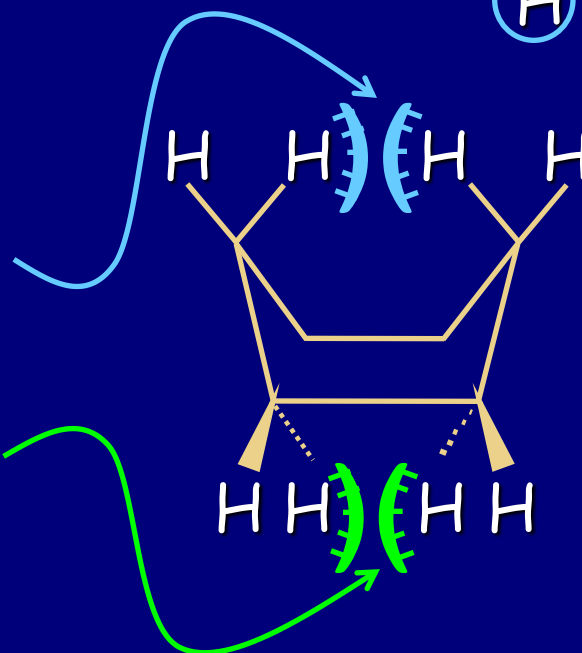
aksijalni(a) i ekvatorijalni(e) položaj

# Promena konformacija cikloheksana



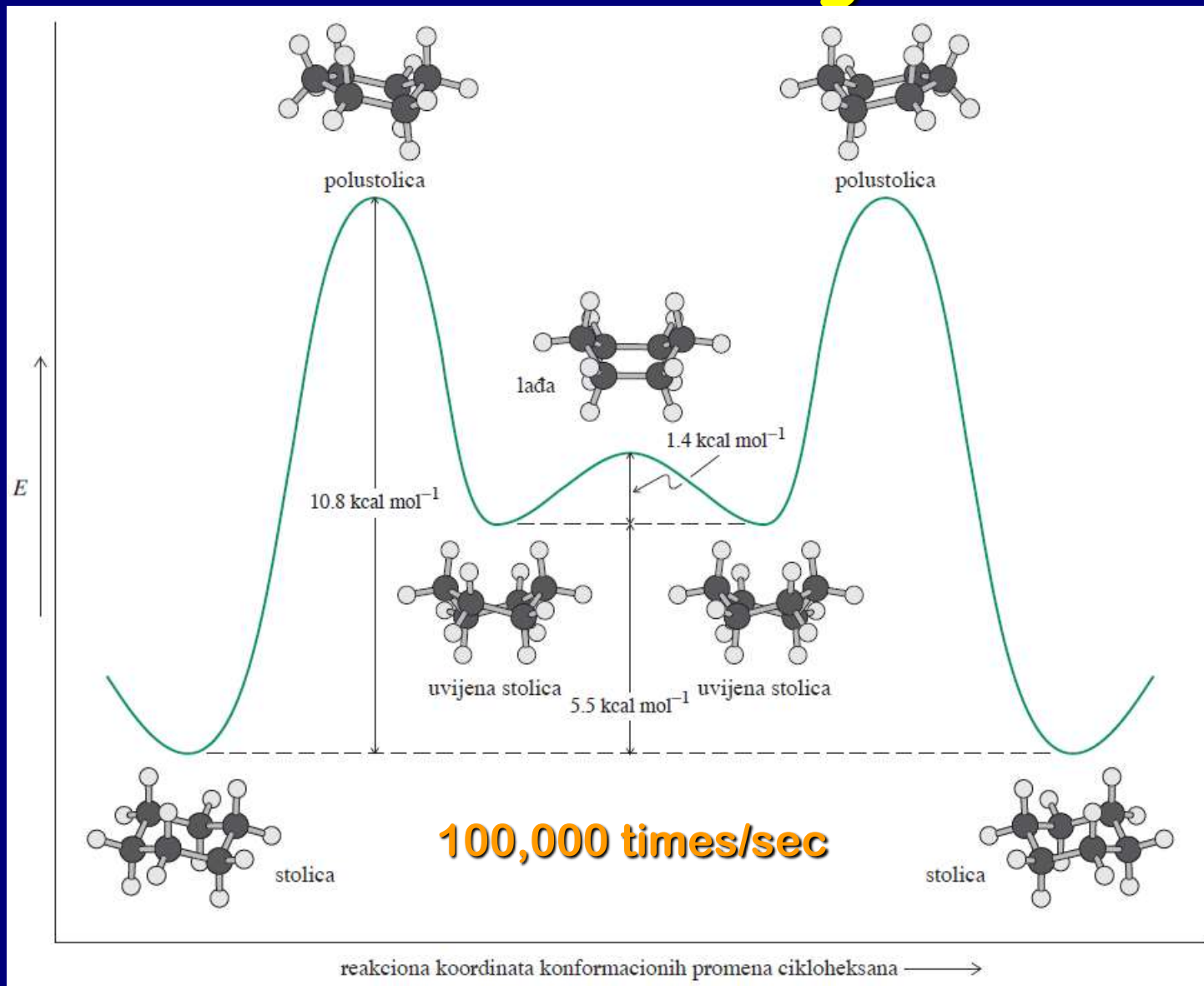
Transanularni  
napon

Eklipsni napon

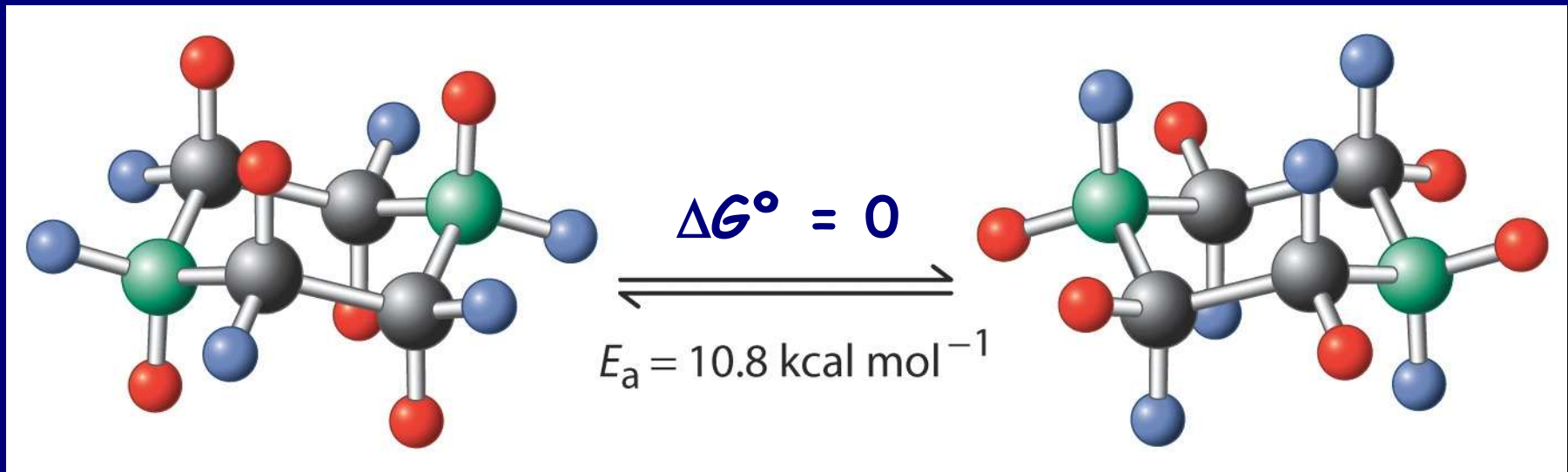


Stolica  $\rightarrow$  Lađa + 6.9 kcal mol<sup>-1</sup>. Lađa je TS.

# Prevođenje jedne konformacije stolice u drugu



# Konformacionom inverzijom aksijalni vodonici se pretvaraju u ekvatorijalne i obrnuto

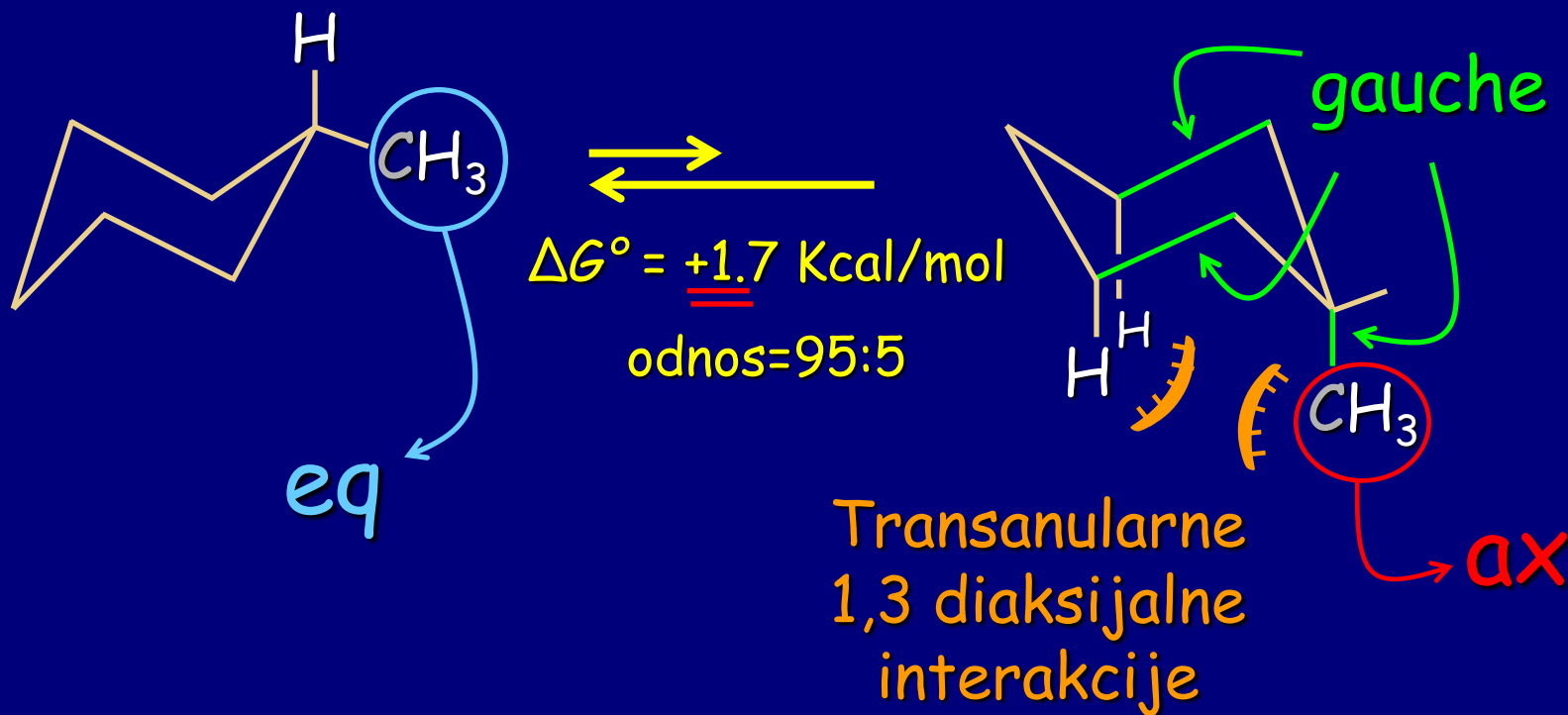


Ove dve strukture su identične.  
Šta se dešava sa supstituisanim cikloheksanima?



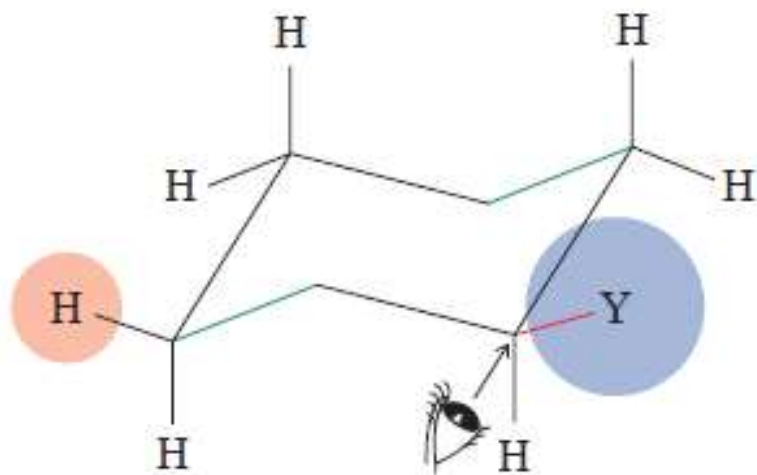
# Supstituisani cikloheksani

Konformaciona analiza: Aksijalni i ekvatorijalni metilcikloheksani nemaju iste energije

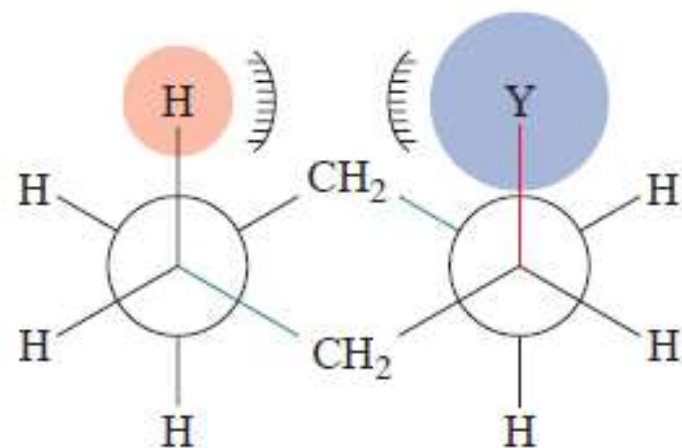
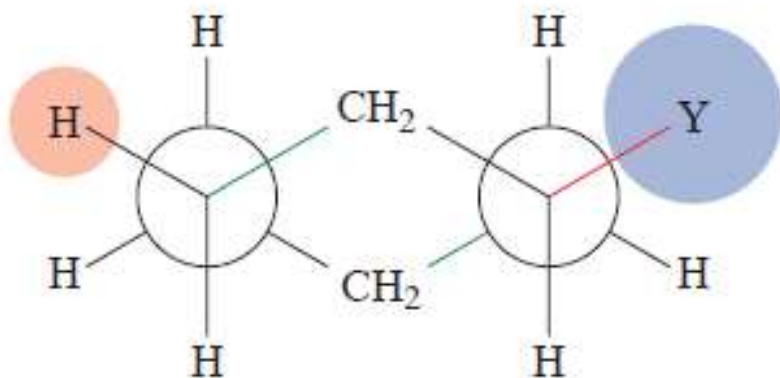
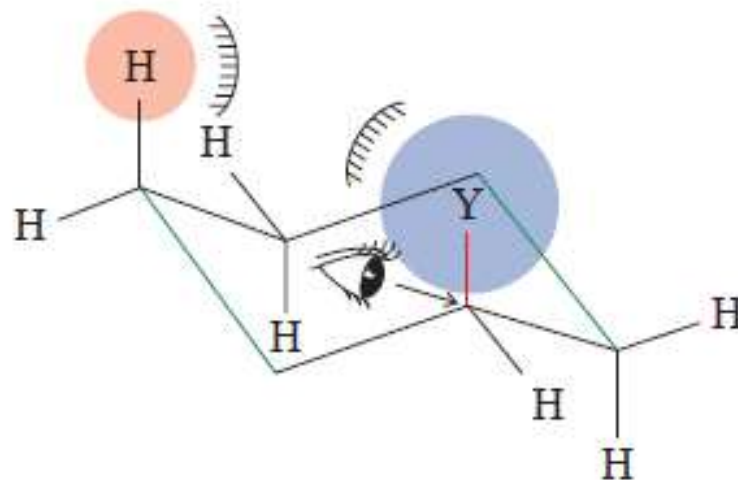


# Aksijalno-ekvatorijalni konformeri

ekvatorijalni Y



aksijalni Y



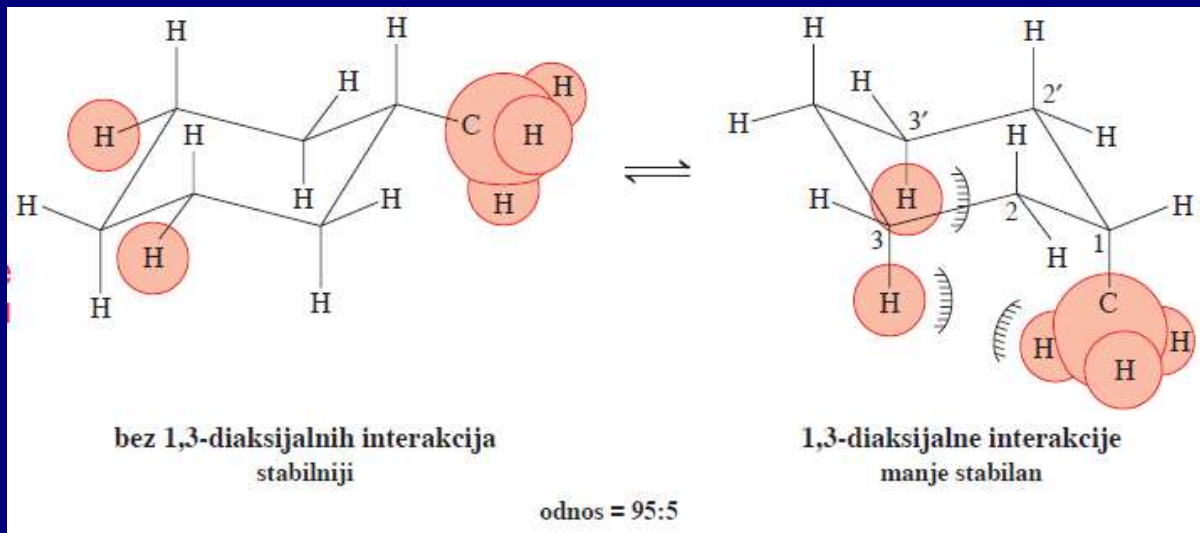
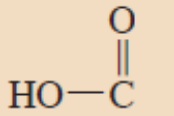
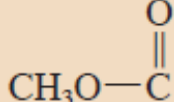


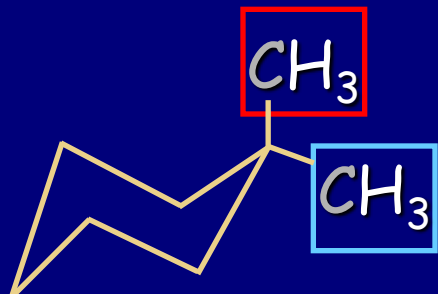
TABELA 4-3

Promene slobodne energije inverzije konformera cikloheksana sa naznačenim ekvatorijalnim supstutentom u konformer sa aksijalnim konformerom

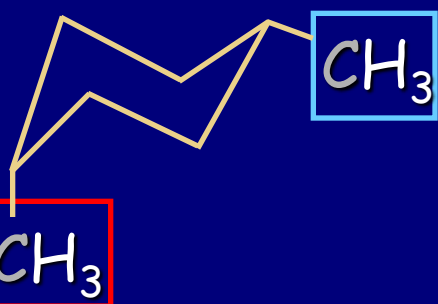
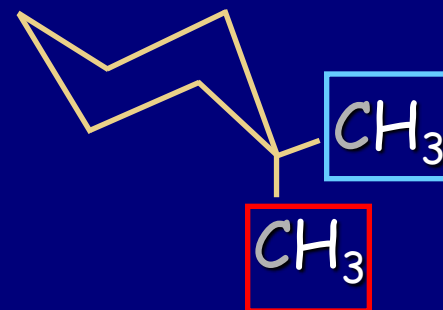
Supstituent	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )	Supstituent	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )
H	0	F	0.25
CH <sub>3</sub>	1.70	Cl	0.52
CH <sub>3</sub> CH <sub>2</sub>	1.75	Br	0.55
(CH <sub>3</sub> ) <sub>2</sub> CH	2.20	I	0.46
(CH <sub>3</sub> ) <sub>3</sub> C	≈ 5	HO	0.94
	1.41	CH <sub>3</sub> O	0.75
	1.29	H <sub>2</sub> N	1.4

Napomena: u svim primerima, stabilniji konformer je onaj u kome je supstituent ekvatorijalan

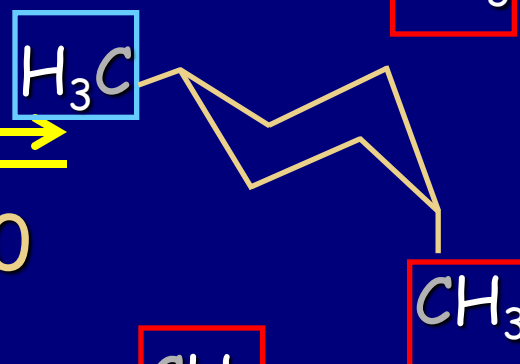
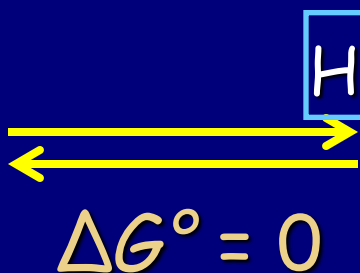
Konformaciona analiza:  $\Delta G^\circ$  mogu biti **aditivne**.  
Razmotrimo dimetilcikloheksane:



1,1-dimetilcikloheksan



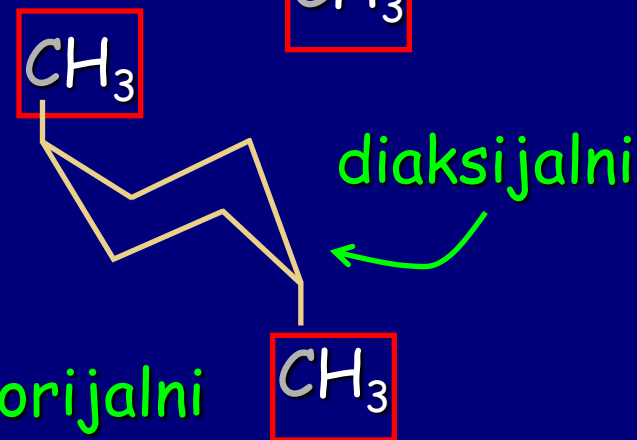
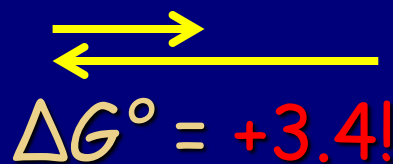
Cis-1,4-dimetilcikloheksan



Ali:

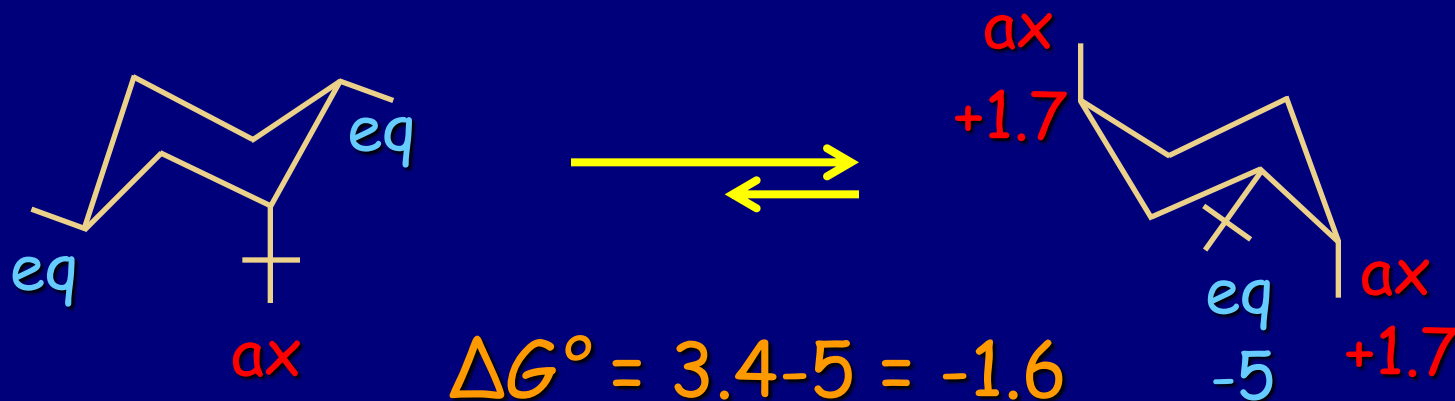


Trans-1,4-dimetilcikloheksan



diekvatorijalni

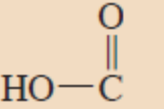
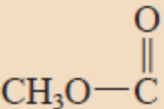
Najveća grupa favorizuje jednu konformaciju:



Veliki supstituenti kao *tert*-Bu, „zaključava“ konformaciju

TABELA 4-3

Promene slobodne energije inverzije konformera cikloheksana sa naznačenim ekvatorijalnim supstuentom u konformer sa aksijalnim konformerom

Supstituent	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )	Supstituent	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )
H	0	F	0.25
CH <sub>3</sub>	1.70	Cl	0.52
CH <sub>3</sub> CH <sub>2</sub>	1.75	Br	0.55
(CH <sub>3</sub> ) <sub>2</sub> CH	2.20	I	0.46
(CH <sub>3</sub> ) <sub>3</sub> C	≈ 5	HO	0.94
	1.41	CH <sub>3</sub> O	0.75
	1.29	H <sub>2</sub> N	1.4

*Napomena:* u svim primerima, stabilniji konformer je onaj u kome je supstituent ekvatorijalan

**Problem:**

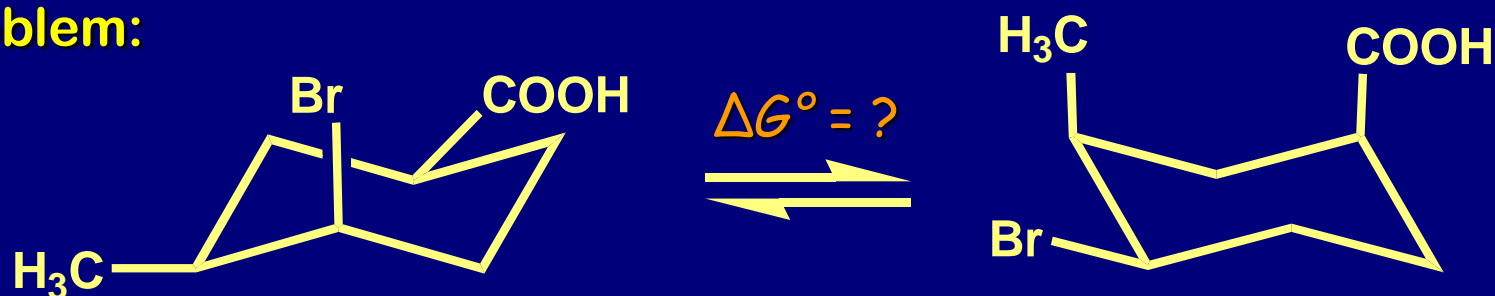
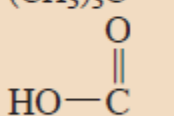
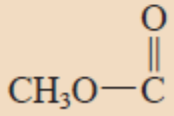
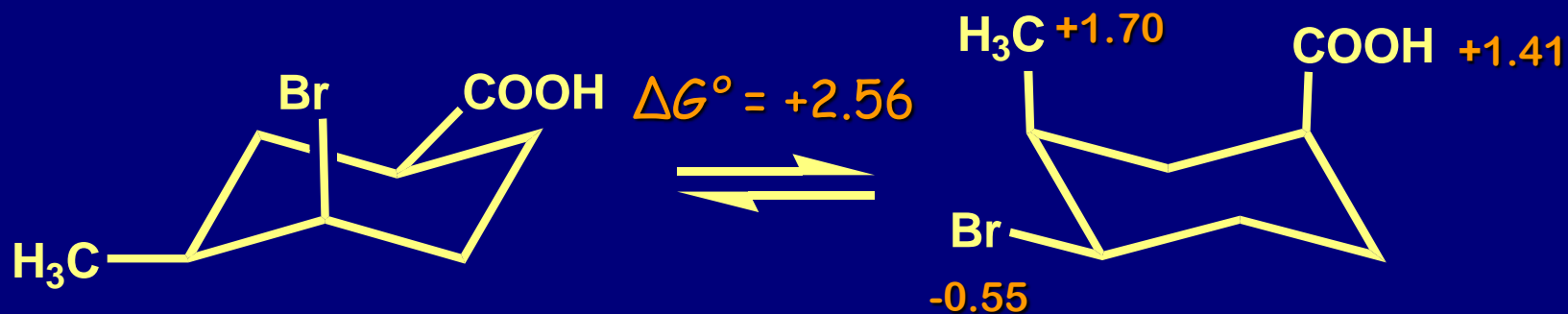


TABELA 4-3

Promene slobodne energije inverzije konformera cikloheksana sa naznačenim ekvatorijalnim supstytutentom u konformer sa aksijalnim konformerom

Supstytutent	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )	Supstytutent	$\Delta G^\circ$ (kcal mol <sup>-1</sup> )
H	0	F	0.25
CH <sub>3</sub>	1.70	Cl	0.52
CH <sub>3</sub> CH <sub>2</sub>	1.75	Br	0.55
(CH <sub>3</sub> ) <sub>2</sub> CH	2.20	I	0.46
(CH <sub>3</sub> ) <sub>3</sub> C	≈ 5	HO	0.94
	1.41	CH <sub>3</sub> O	0.75
	1.29	H <sub>2</sub> N	1.4

*Napomena:* u svim primerima, stabilniji konformer je onaj u kome je supstytutent ekvatorijalan

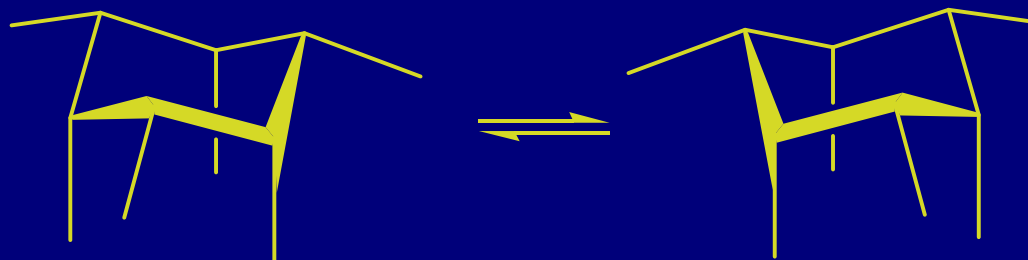


**TABLE 4-4**

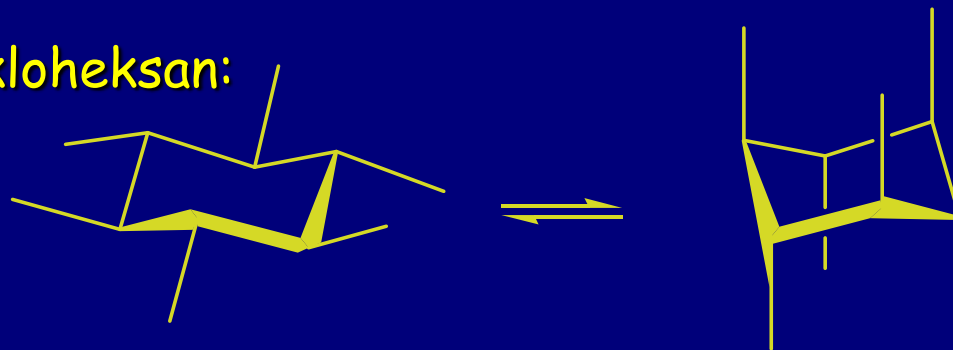
**Relation of Cis-Trans Stereochemistry in Substituted Cyclohexanes to Equatorial-Axial Positions in the Two-Chair Forms**

<i>cis</i> -1,2	Axial-equatorial	Equatorial-axial
<i>trans</i> -1,2	Axial-axial	Equatorial-equatorial
<i>cis</i> -1,3	Axial-axial	Equatorial-equatorial
<i>trans</i> -1,3	Axial-equatorial	Equatorial-axial
<i>cis</i> -1,4	Axial-equatorial	Equatorial-axial
<i>trans</i> -1,4	Axial-axial	Equatorial-equatorial

*sve-cis*-heksametilcikloheksan:



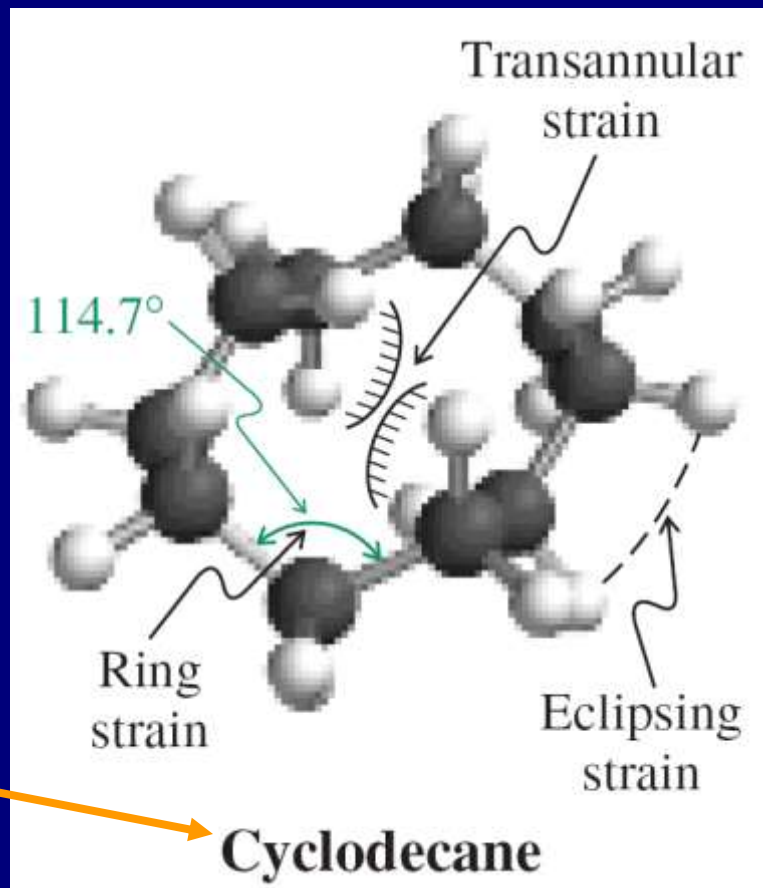
*sve-trans*-heksametilcikloheksan:





# Srednji prstenovi: transannularne interakcije

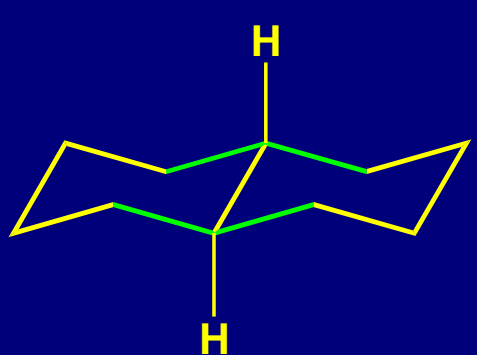
Ring size ( $C_n$ )	Total strain
3	27.6
4	26.3
5	6.5
6	0.1
7	6.4
8	10.0
9	12.9
10	14.0
11	11.0
12	2.4
14	0.0



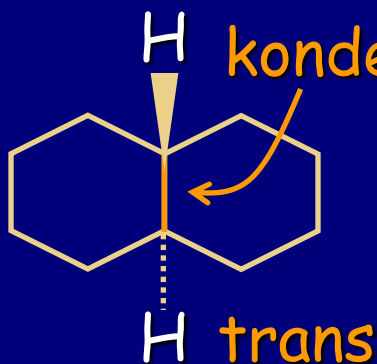
# Biciklični, kondenzovani, policiklični, polihedralni alkani



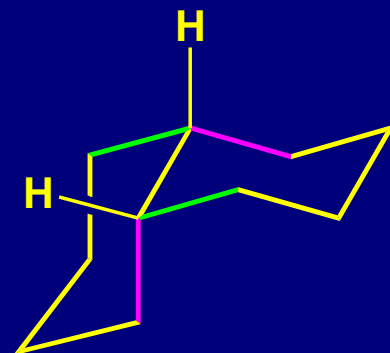
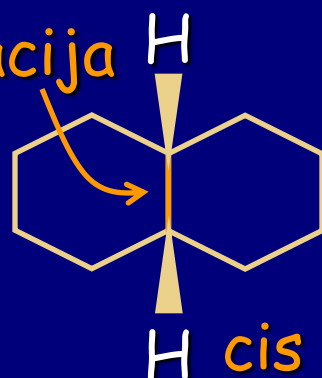
biciklo[2.2.1]heptan  
(norbornan)



ekvatorijalne C-C veze  
trans-dekalin



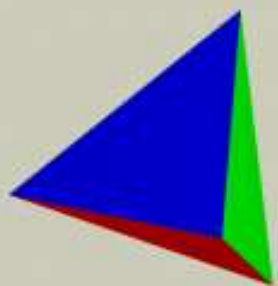
Biciklo[4.4.0]dekan  
(dekalin), trans i cis



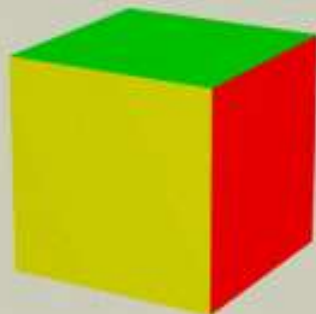
aksijalne C-C veze  
ekvatorijalne C-C veze  
cis-dekalin

Napraviti model i pokušati konformacionu inverziju!!!!

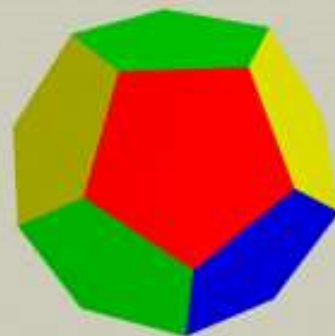
# Ugljovodonici sa naponom: Da li postoji granica? Egzotični poliedri: Pet Platonskih ili kosmička čvrsta tela (Platon 350 BC)



**Tetrahedran**  
(vatra)

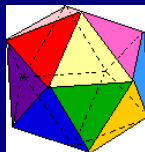


**Kuban**  
(zemlja)

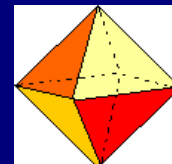


**Dodekahedron**  
("eter")

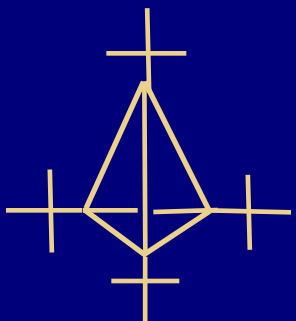
ikosahedron (voda)



oktahedron (vazduh)

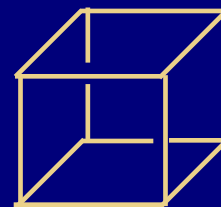


Da li je moguće napraviti Platonska tela sa ugljeničnim skeletom  $(CH)_n$ ?



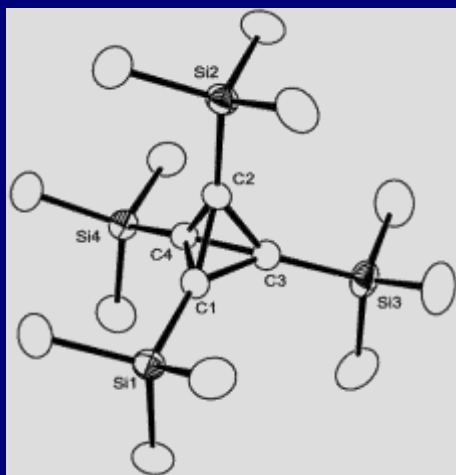
m.p. 135°C !  
Strain:  
130 kcal  
mol<sup>-1</sup>

Maier, 1978,  
tetra-*t*-Bu-  
tetrahedrane.  
Substituted C<sub>4</sub>H<sub>4</sub>



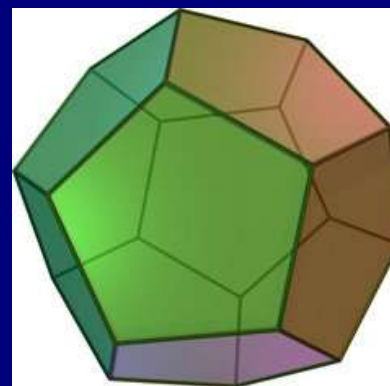
m.p. 126°C  
Strain:  
166 kcal  
mol<sup>-1</sup>

Eaton, 1964,  
cubane, C<sub>8</sub>H<sub>8</sub>




m.p. 202°C

Maier, Sekiguchi, 2002,  
tetrakis(trimethylsilyl)-  
tetrahedrane.

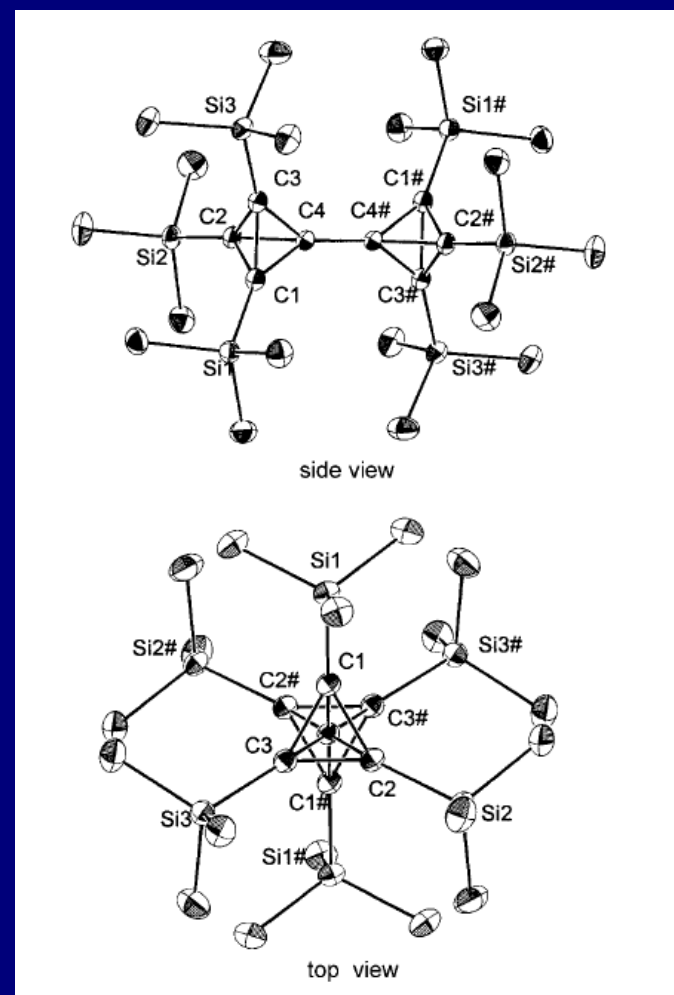
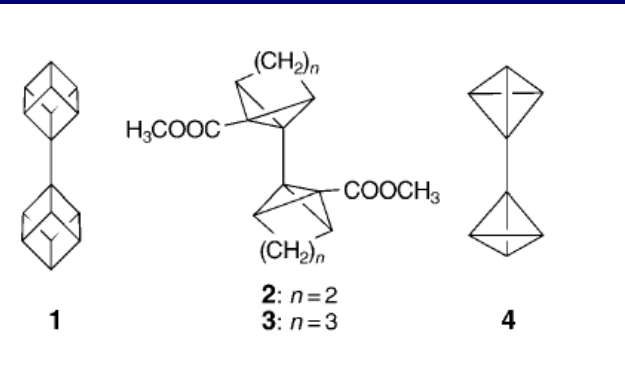
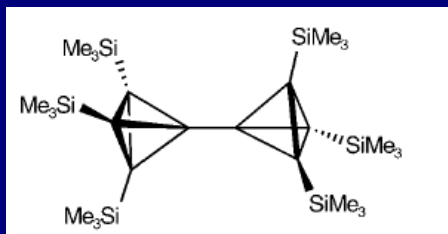


m.p.  
430°C !

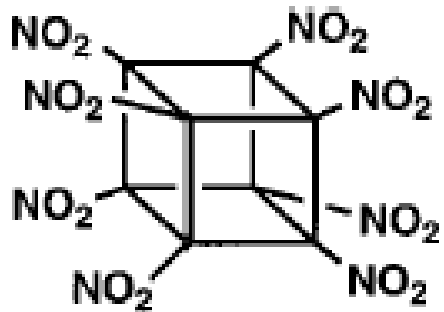
Strain:  
60 kcal  
mol<sup>-1</sup>

Paquette, 1982,  
dodecahedrane, C<sub>20</sub>H<sub>20</sub>,  
12  faces

Sekiguchi, Angew. 2005, 5821



# Oktanitrokuban: Novi eksploziv i raketno gorivo

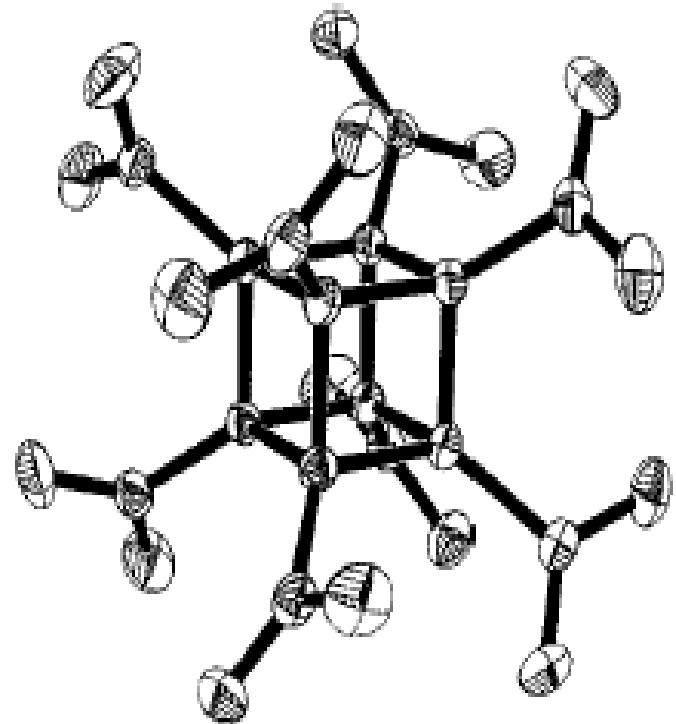


OCTANITROCUBANE



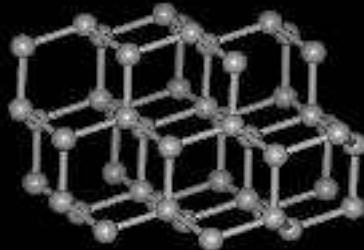
VOLUME EXPANSION ~ 1150 fold @ STP

ENERGY RELEASE ~ 830 kcal/mole

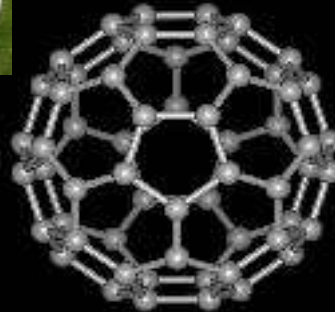


*Eaton, Adv. Mat., 2000.*

# Alotropi ugljenika: $C_n$

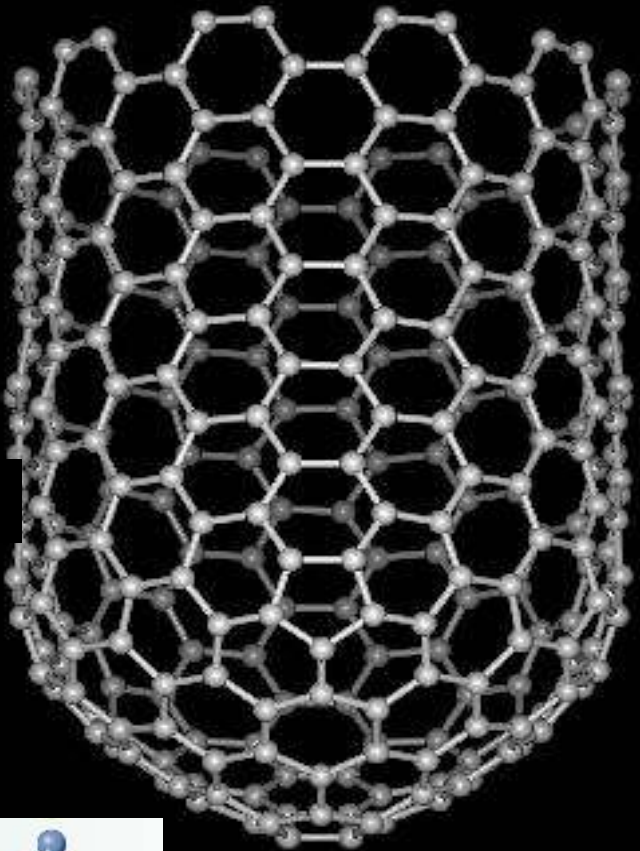


diamond

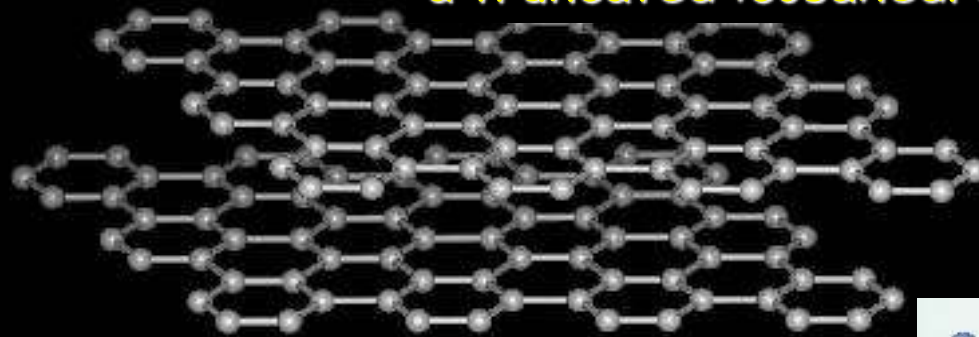


$C_{60}$

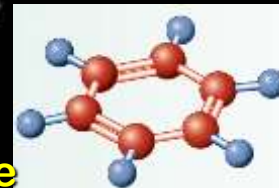
"buckminsterfullerene"  
a truncated icosahedron



(10,10) tube



graphite



Benzene

# Atomic Resolution Imaging of a Carbon Nanotube

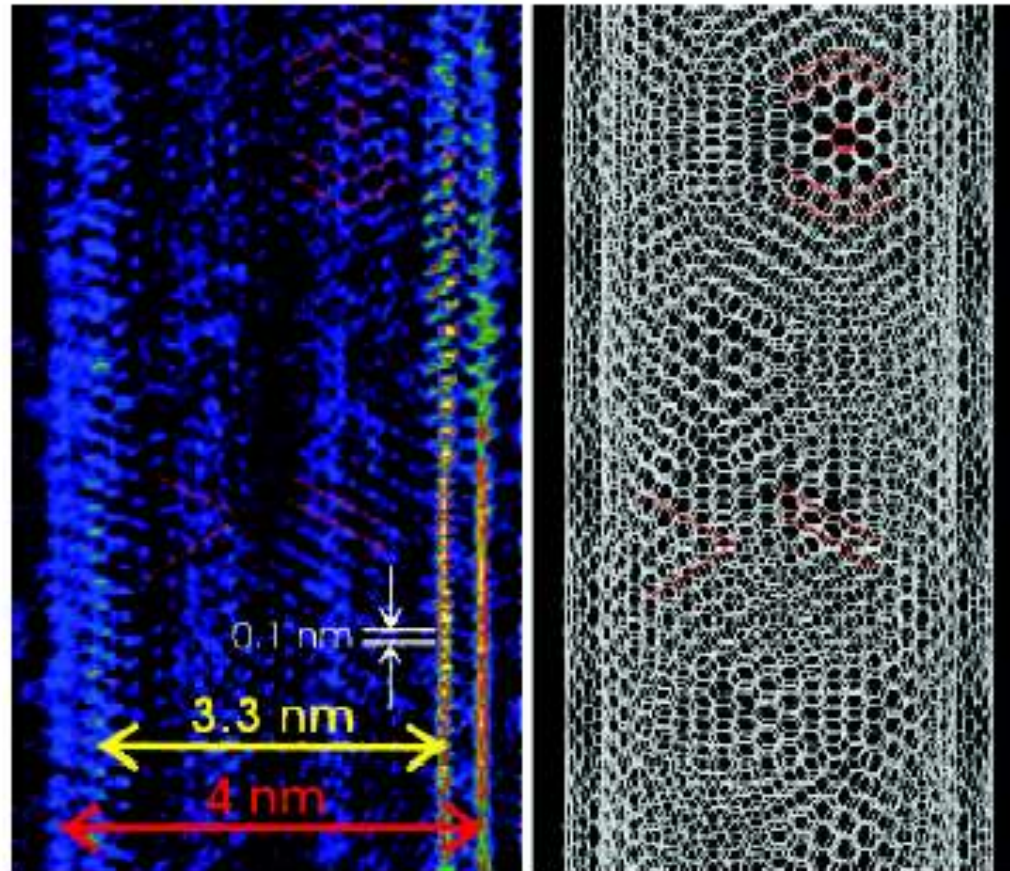
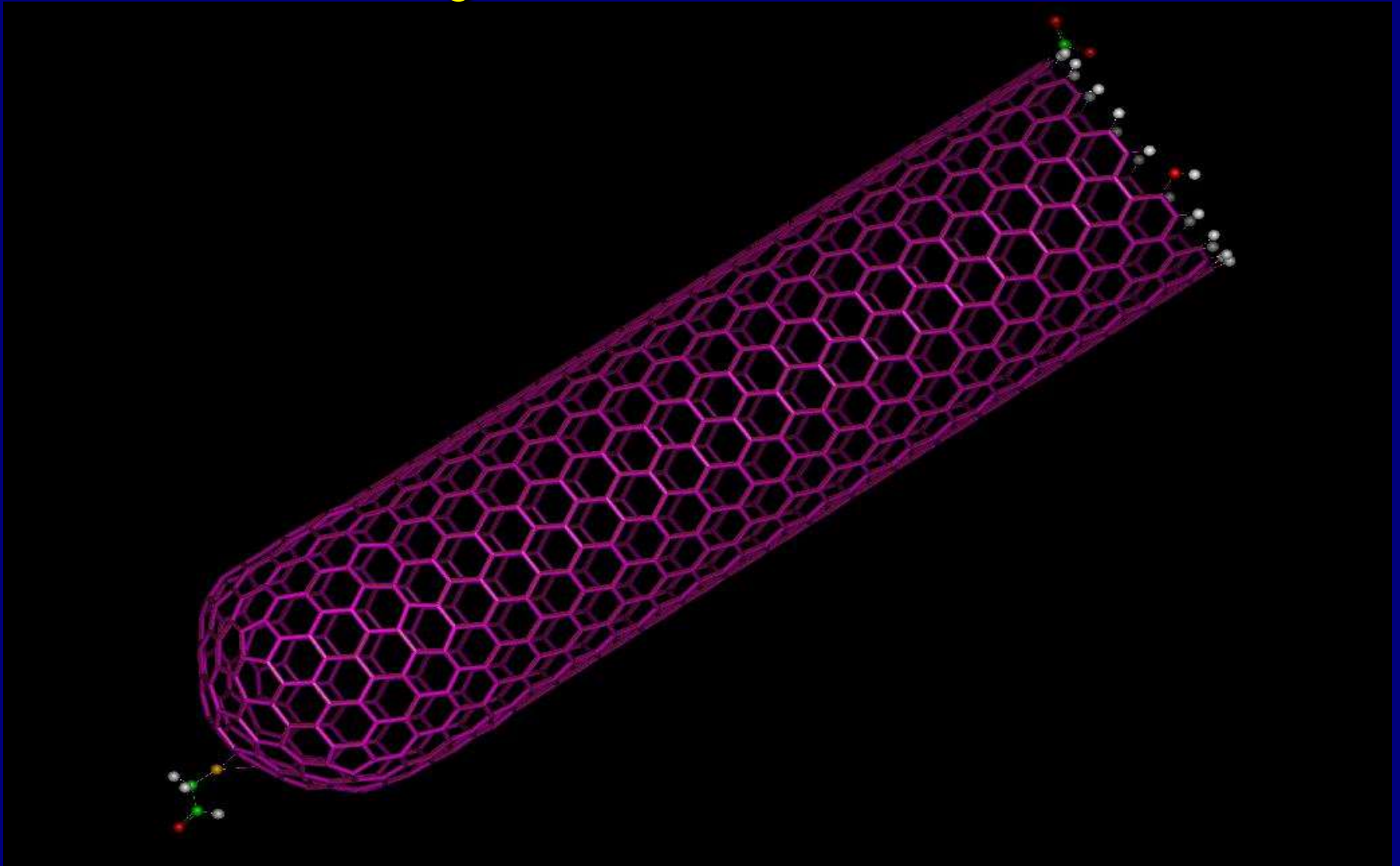


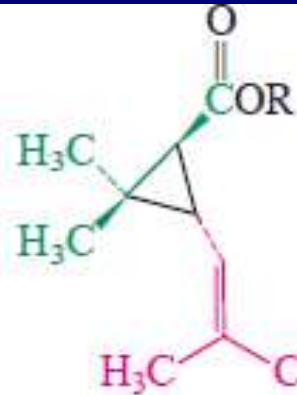
Fig. 2. (left) A section of the reconstructed DWNT image at 1-Å resolution and (right) a structural model constructed with the use of the chiral vectors of (35, 25) and (26, 24) that were determined from the image and diffraction pattern. The DWNT imaged here is one of many in our catalytic chemical vapor deposition-grown samples. Yellow and red lines mark the diameters of the inner and outer tubes, respectively. One side of walls is stronger than the other, which is because of the illumination. The DWNT is incommensurate. In projection, the structure has complex patterns showing both accidental coincidences and Moiré fringes, which are highlighted by hexagons and lines.



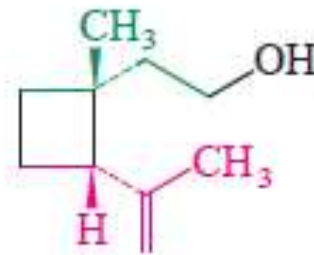
# Ugljenične nanotube: novi materijali za budućnost



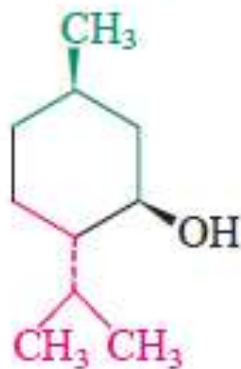
# Karbociklični proizvodi u prirodi



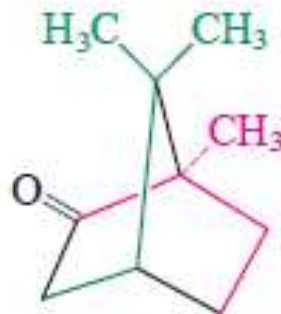
*trans*-hrizontemska kiselina (R= H)  
*trans*-hrizontemski estari (R ≠ H)



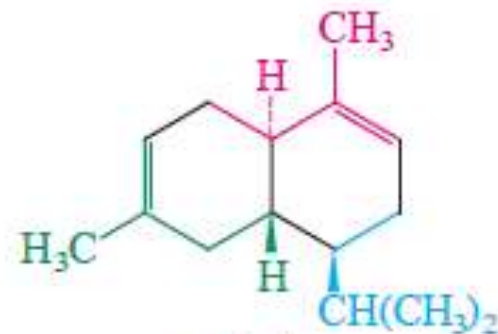
grandizol



mentol

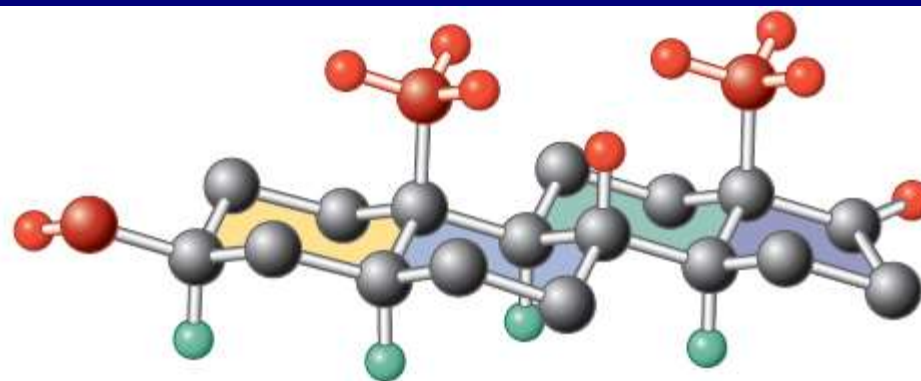
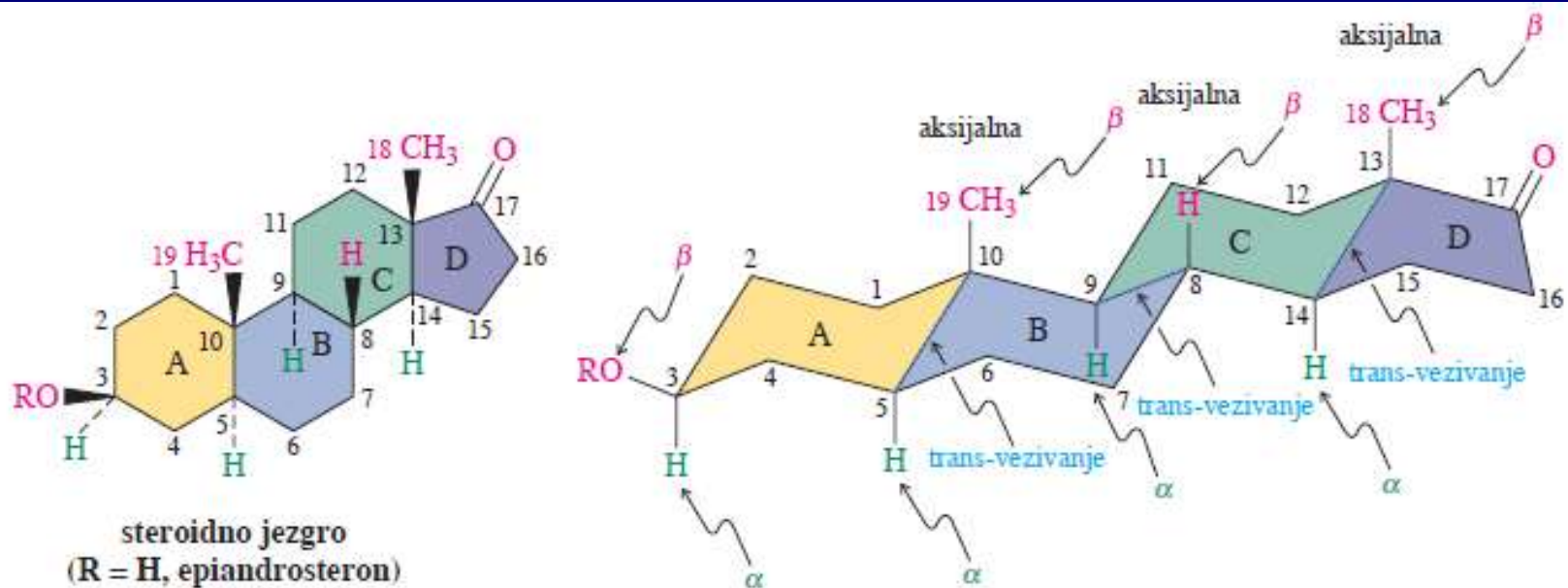


kamfor

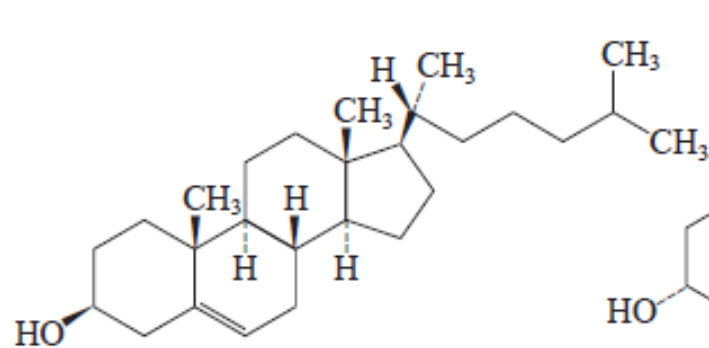


$\beta$ -kadinen

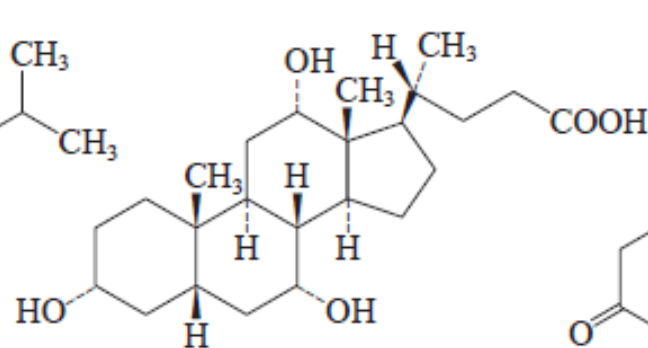
# Steroidi: tetraciklični proizvodi



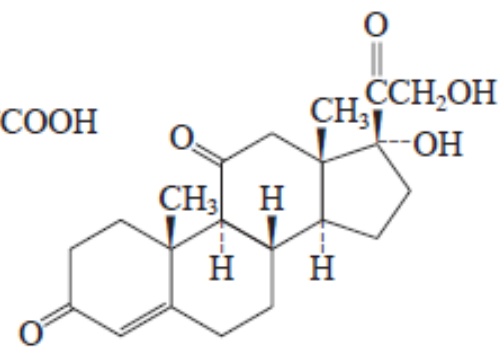
epiandrosteron



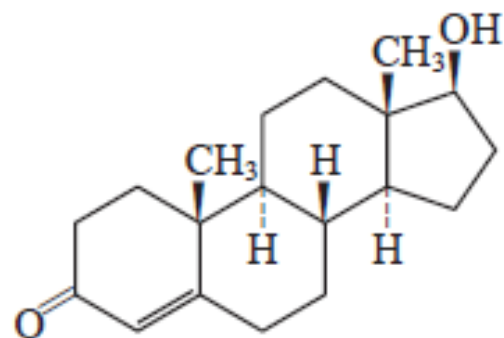
holesterol



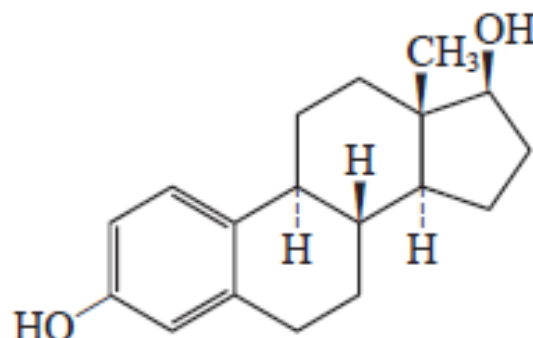
holna kiselina



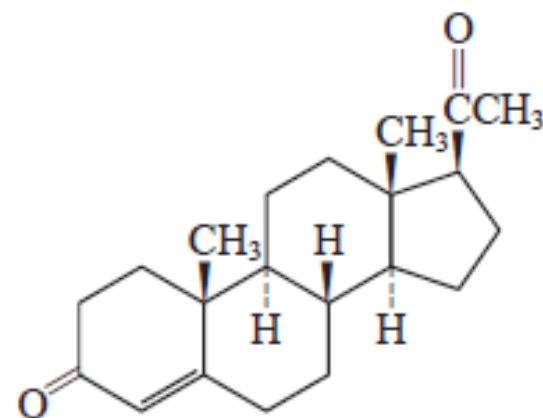
kortizon



testosteron



estradiol



progesteron

## Vežba 4-2

Napišite strukture i imena drugih pet izomernih brommetil-cikloheksana.

## Vežba 4-3

*Trans*-1,2-dimetilciklopropan je stabilniji od *cis*-1,2-dimetilciklopropana. Zašto? Nacrtajte formule da ilustrujete svoj odgovor. Koji izomer oslobađa više toplote prilikom sagoravanja?

## Vežba 4-4

Nacrtajte Newman-ove projekcije veza ugljenik-ugljenik ciklopropana, ciklobutana i ciklopentana u njihovim najstabilnijim konformacijama. Koristite modele koje ste napravili rešavajući vežbu 4-1 i pomozite se slikom 4-6. Koliki su približni torzioni uglovi između C-H veza kod svakog od njih?

## Vežba 4-7

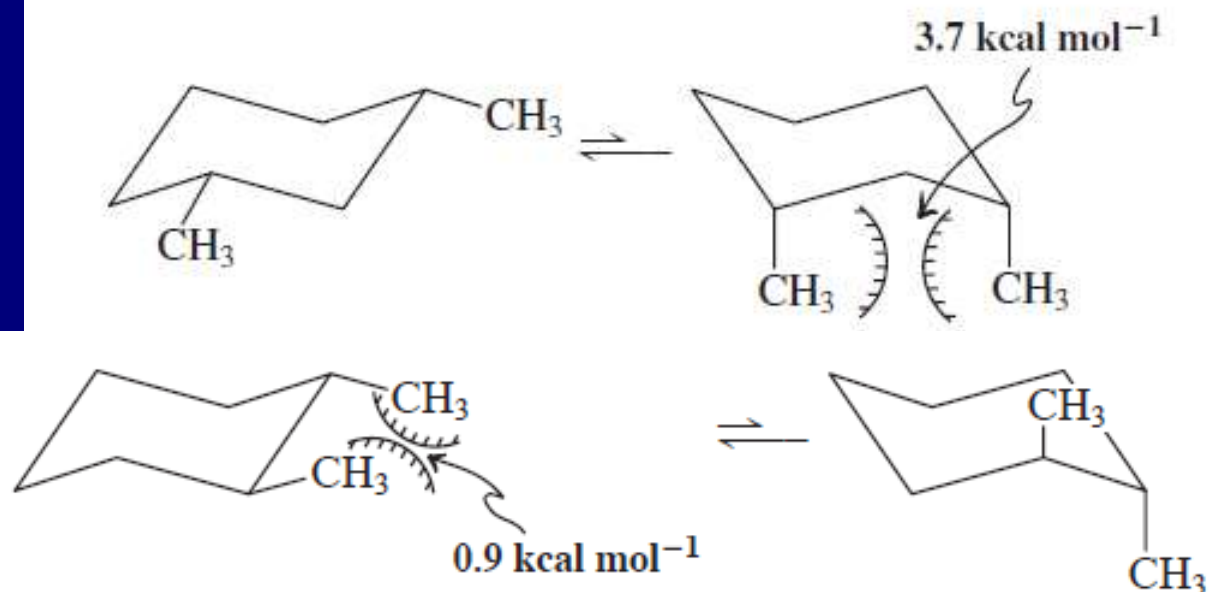
Izračunajte  $\Delta G^\circ$  ravnoteže dve stoličaste konformacije (a) 1-etil-1-metilcikloheksana; (b) *cis*-1-etil-4-metilcikloheksana; (c) *trans*-1-etil-4-metilcikloheksana.

## Vežba 4-8

Nacrtajte obe konformacije stolice svakog od datih izomera: (a) *cis*-1,2-dimetilcikloheksan; (b) *trans*-1,2-dimetilcikloheksan; (c) *cis*-1,3-dimetilcikloheksan; (d) *trans*-1,3-dimetilcikloheksan. Koji od ovih izomera uvek ima jednak broj aksijalnih i ekvatorijalnih supstituenata? Koji postoje kao ravnotežna smeša diaksijalnih i diekvatorijalnih oblika?

## Vežba 4-9

Iako su vrednosti za supstituente iz tabele 4-3 aditivne i mogu biti upotrebljene za ukazivanje položaja ravnoteže između dva konformera supstituisanog cikloheksana, izmerene vrednosti  $\Delta G^\circ$  mogu biti zbunjujuće zbog dodatnih 1,3-diaksijalnih i 1,2-*gauche*-interakcija između grupa. Na primer, *trans*-1,4-dimetilcikloheksan i njegovi izomeri *cis*-1,3- i *trans*-1,2-dimetilcikloheksani postoje kao ravnotežna smeša diekvatorijalno-diaksijalnih oblika i zato bi trebalo da imaju iste vrednosti  $\Delta G^\circ = 3,4 \text{ kcal mol}^{-1}$ . Međutim, izmerene vrednosti su veće ( $5,4 \text{ kcal mol}^{-1}$ ) za prvi, a manje ( $2,5 \text{ kcal mol}^{-1}$ ) za drugi izomer. Objasnite. (**Pomoć:** u slučaju *cis*-1,3-dimetilcikloheksana pažljivo analizirajte sve 1,3-diaksijalne interakcije i uporedite sa odgovarajućim interakcijama kod *trans*-1,4-dimetilcikloheksana. U analizi *trans*-1,2-izomera uzmite u obzir blizinu dve metil-grupe; podsetite se *gauche-anti* odnosa kod butana, odeljak 2-8.)

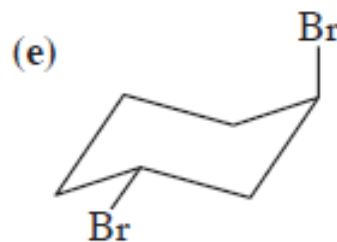
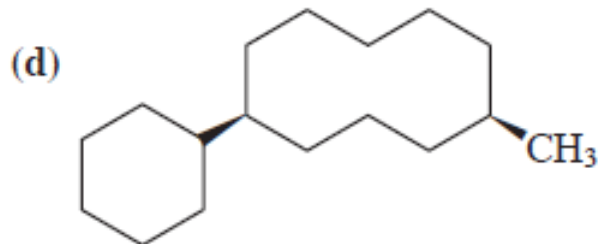
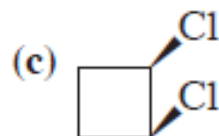
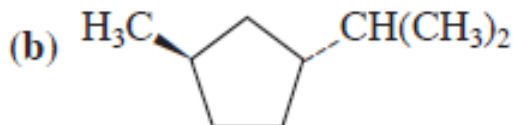
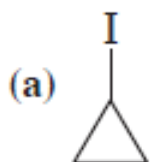


## Vežba 4-11

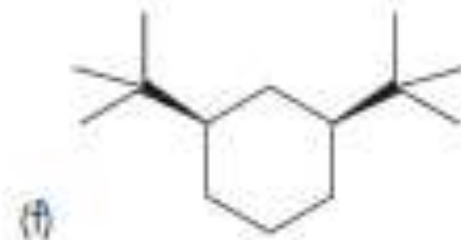
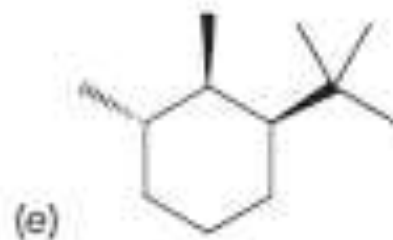
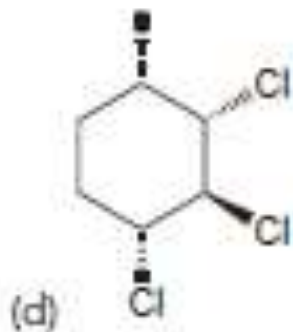
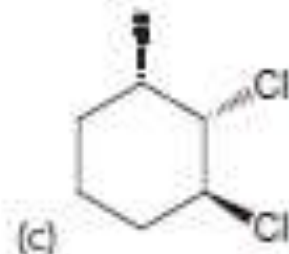
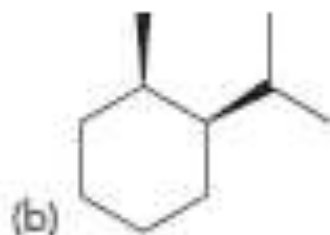
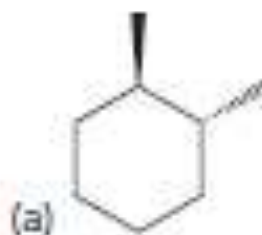
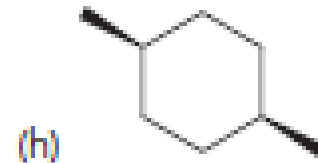
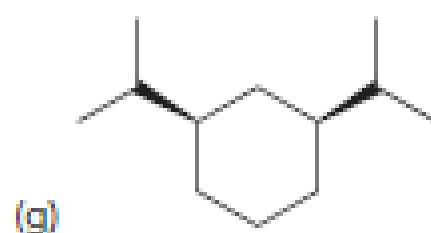
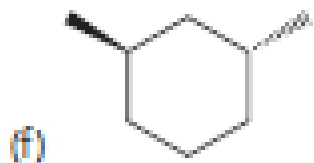
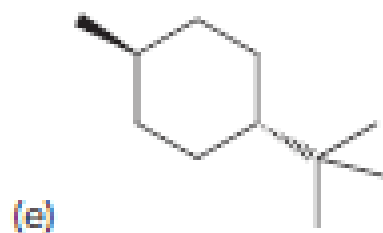
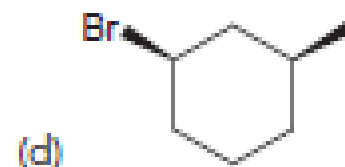
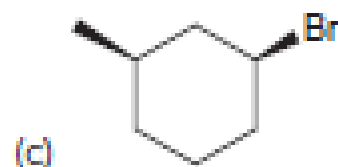
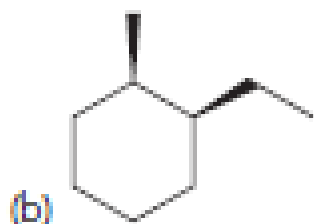
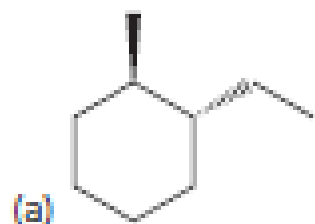
Nacrtajte stabilniju stoličastu konformaciju mentola.

16. Nacrtajte što više struktura koje imaju formulu  $C_5H_{10}$  i sadrže jedan prsten. Imenujte ih.

17. Imenujte date molekule prema IUPAC-ovom sistemu.



# Prikazati sledeća jedinjenja u najstabilnijim konformacijama:





Za svaki par izomera a-d odrediti koje jedinjenje je stabilnije (nacrtati odgovarajuće konformacije stolice):

