Лекция 4
Циклоалканы

- *Si sapis, sis apis* –
- Если ты разумен, будь пчелой(трудись)

- Циклоалканы и их производные. Классификация алициклов.
- Энергия напряжения циклоалканов и ее количественная оценка на основании сравнения теплот образования и теплот сгорания циклоалканов и соответствующих алканов.
- Типы напряжения в циклоалканах и подразделение циклов на малые, средние циклы и макроциклы.
- Строение циклопропана, циклобутана, циклопентана, циклогексана.
- Конформационный анализ циклогексана. Аксиальные и экваториальные связи в конформации "кресло" циклогексана.

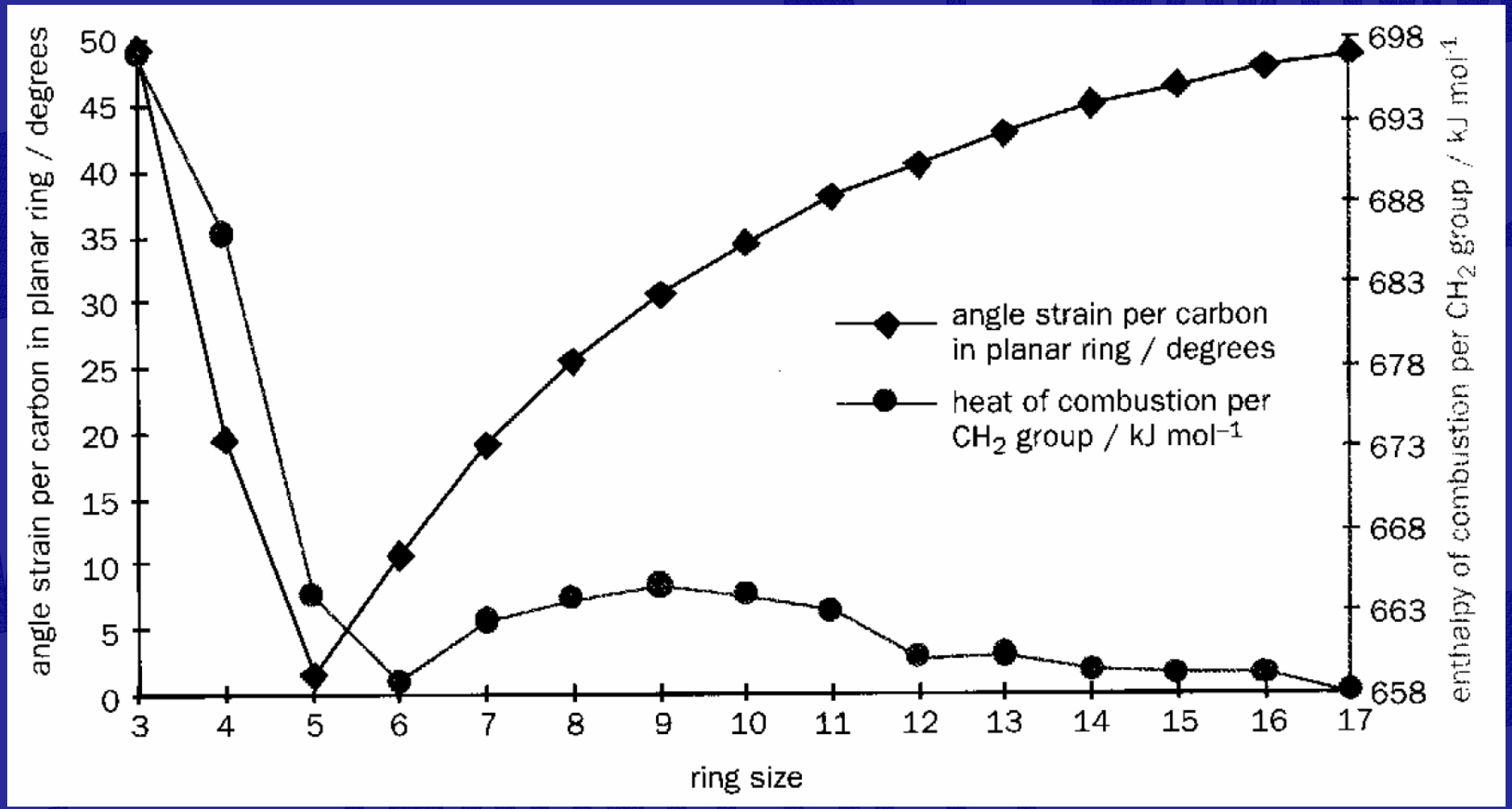
Число атомов	Внутренний угол в планарном кольце	отклонение (109.5°)
3	60°	49.5°
4	90°	19.5°
5	108°	1.5°
6	120°	-10.5°
7	128.5°	-19°
8	135°	-25.5°

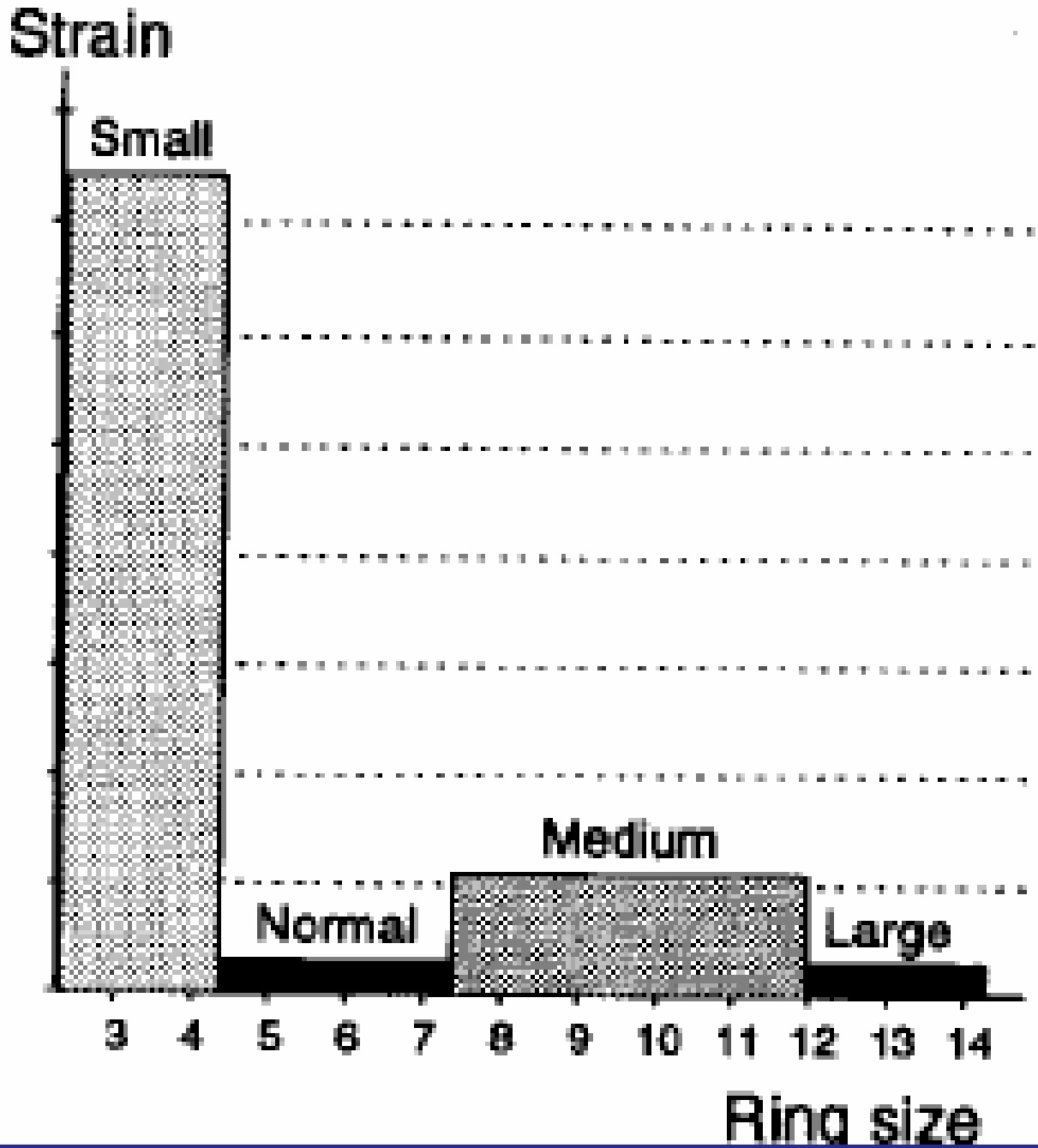
Теплоты сгорания н-алканов

Алкан	n =	$-\Delta H_c$, ккал/моль	Разница, ккал/моль
Этан	0	371.4	157.2
Пропан	1	528.6	156.4
Бутан	2	685	156.9
Пентан	3	841.9	157.1
Гексан	4	999	157.1
Гептан	5	1155.5	156.5
Октан	6	1312.1	156.6

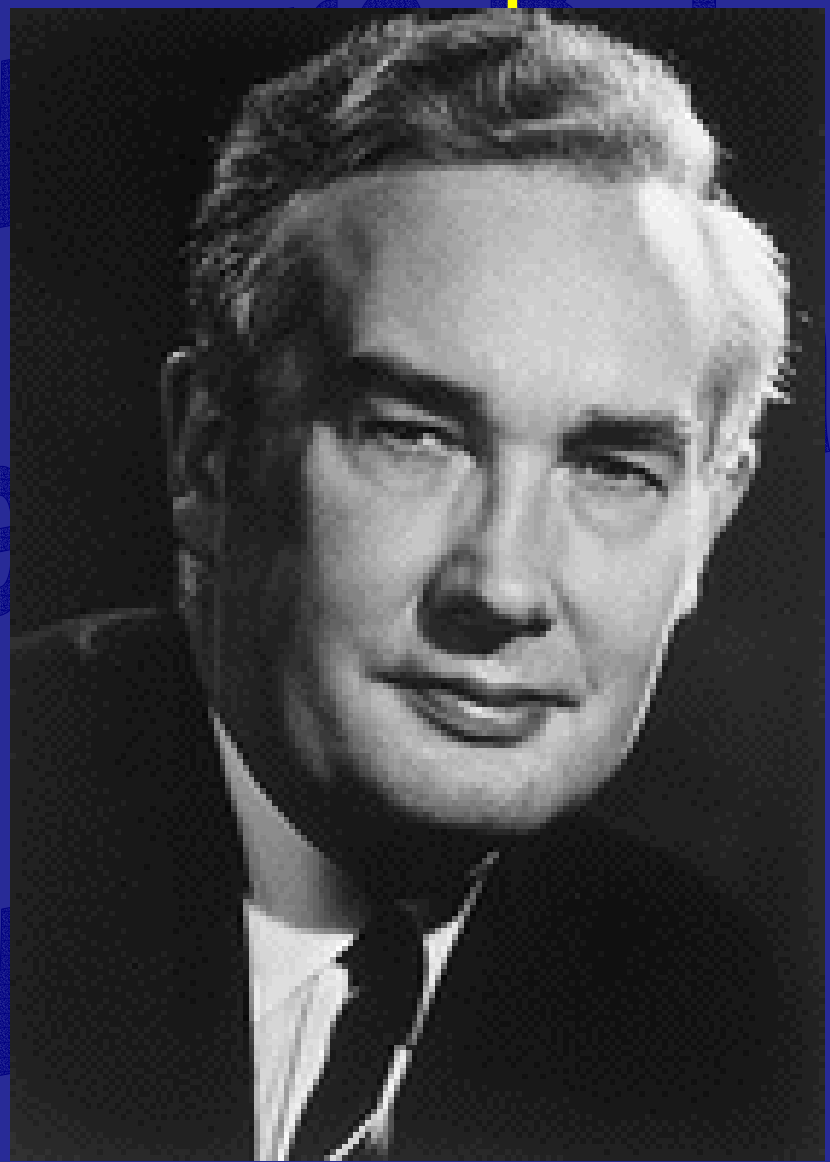
Теплоты сгорания циклоалканов (на одну CH2 группу)

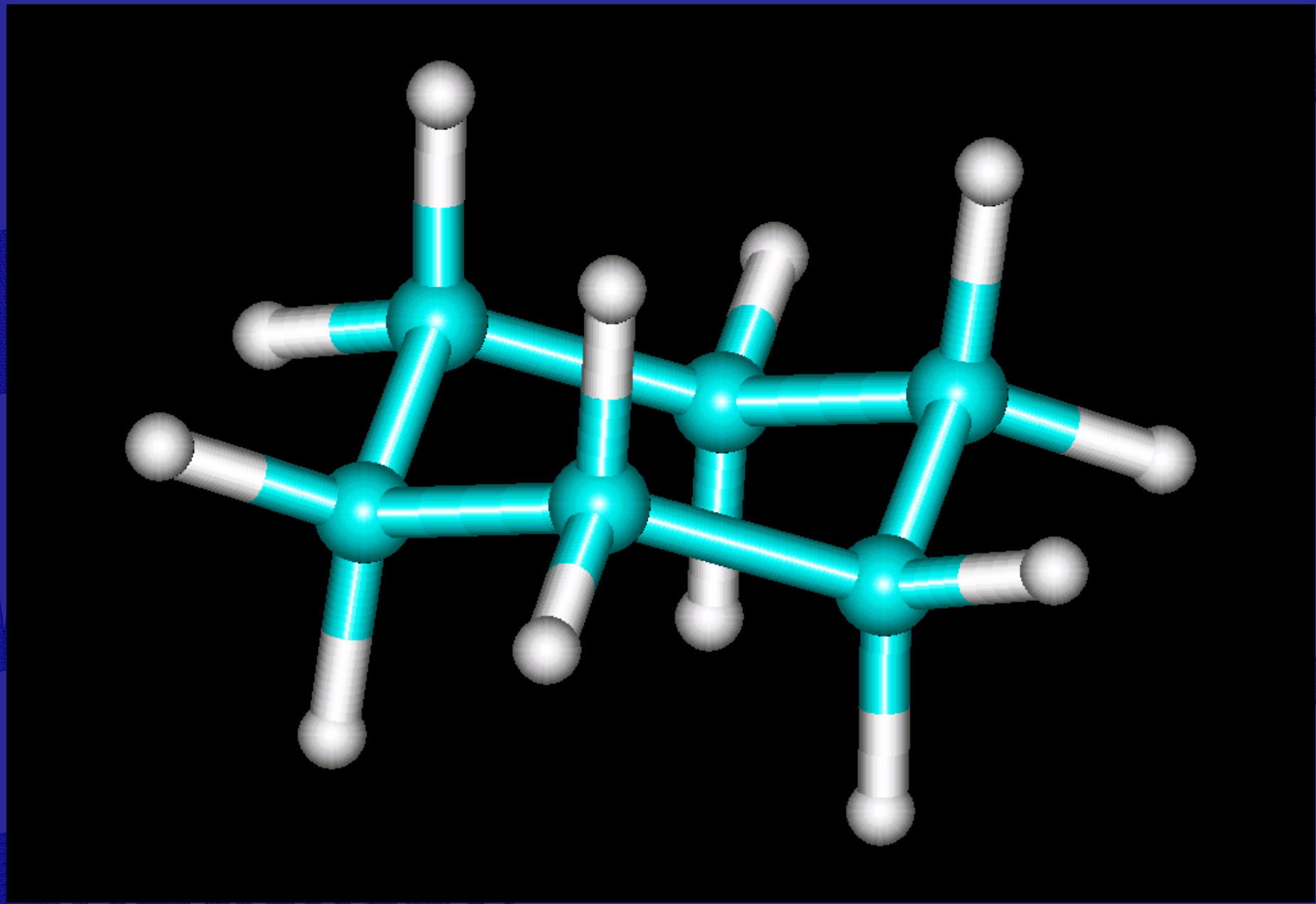
n	$-\Delta H_c$, ккал/моль	n	$-\Delta H_c$, ккал/моль
3	166.3	10	158.6
4	163.9	11	158.4
5	158.7	12	157.8
6	157.4	13	157.7
7	158.3	14	157.4
8	158.6	15	157.5
9	158.8	16	157.5


angle strain per carbon in planar ring / degrees
enthalpy of combustion per CH_2 group / kJ mol^{-1}
ring size
angle strain per carbon in planar ring / degrees
heat of combustion per CH_2 group / kJ mol^{-1}
0
5
10
15
20
25
30
35
40
45
50
658
663
668
673
678
683
688
693
698
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

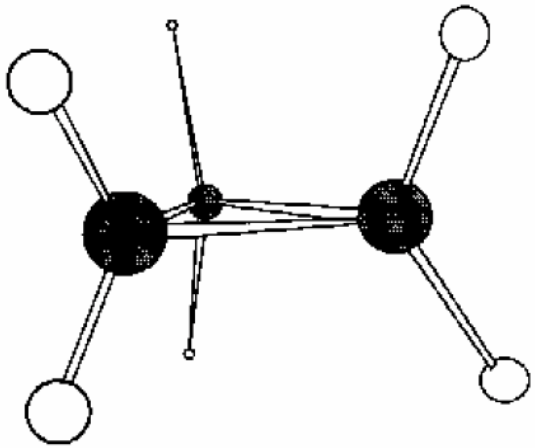

Strain
Small
Medium
Normal
Large
3
4
5
6
7
8
9
10
11
12
13
14
Ring size

Д. Бартон (1918-1998)
Нобелевская премия 1969г.



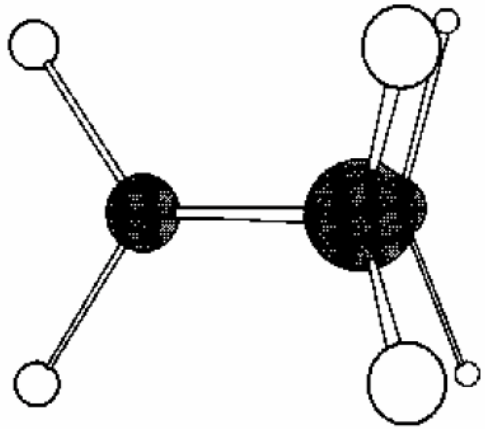


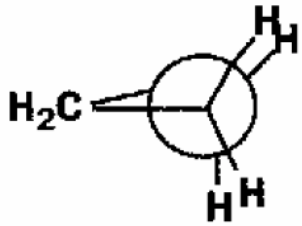
Циклогексан в конформации кресла



a side-on view of cyclopropane

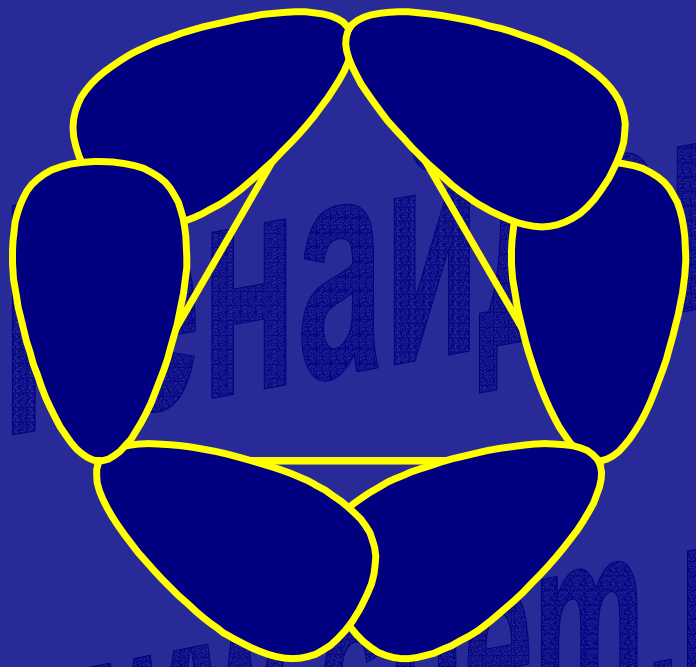
view along C–C

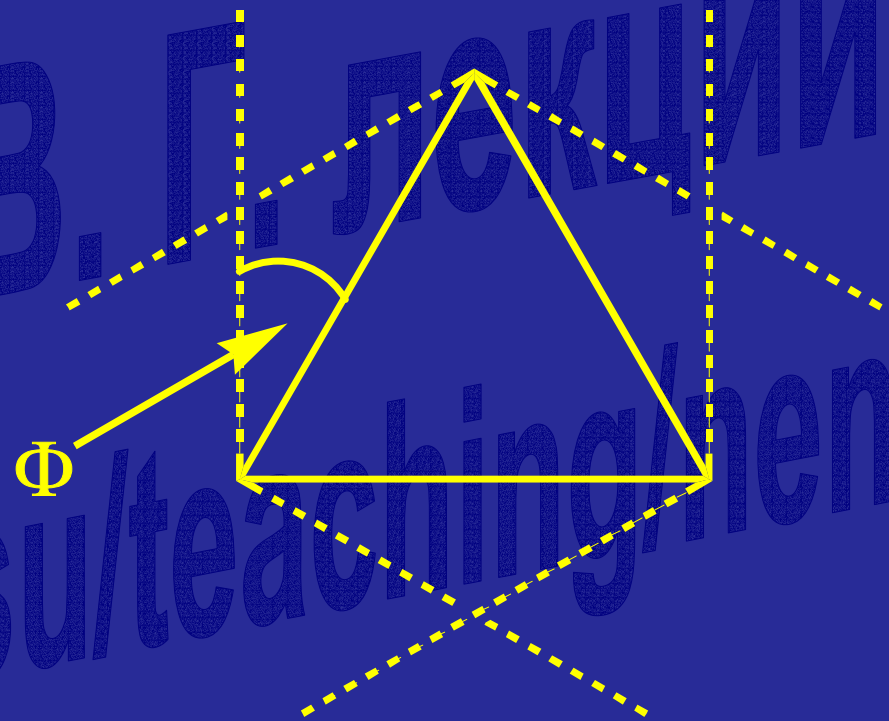




viewing cyclopropane (almost) along a C–C bond shows that all the C–H bonds are eclipsed

	циклопропан	этан	этилен	ацетилен
угол H-C-H, °	118	109.5	120	-
r(C-H), пм	108	110.3	108.6	105.7
r(C-C), пм	154	154	134	120
ν(C-H), $см^{-1}$	3000, 3062	2960, 2860	3010-3060	3300
угол H-C-C, °	116,4	109.5	120	180
		→ увеличение "s" характера C-H связи →		

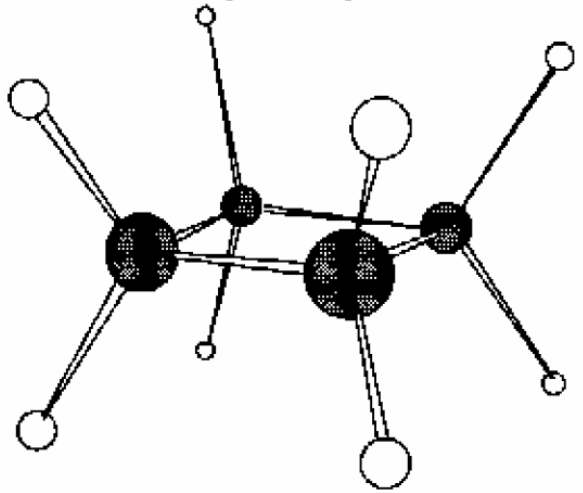




C-C связь имеет больший p характер sp^5

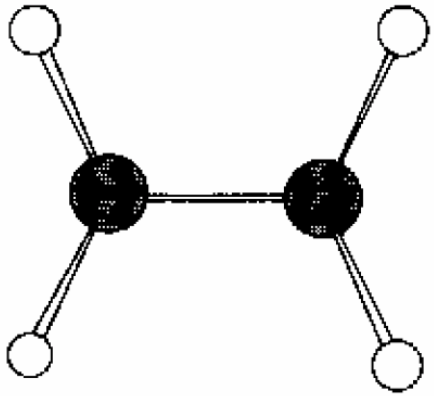
C-H связь имеет больший s характер sp^2

Φ = 21 градус

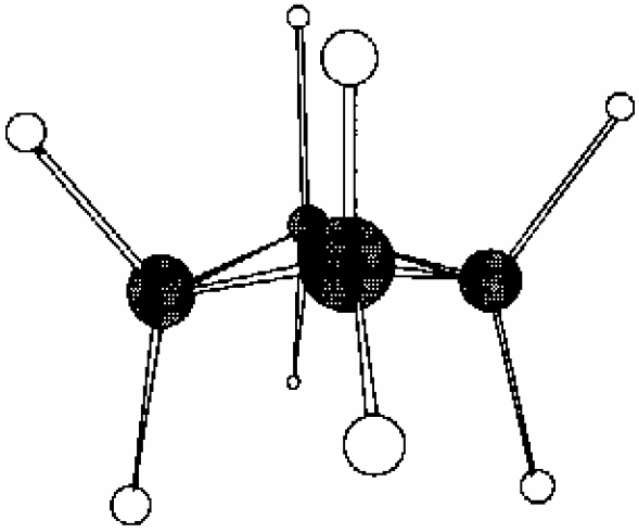


planar cyclobutane (not the real conformation)

view along C–C

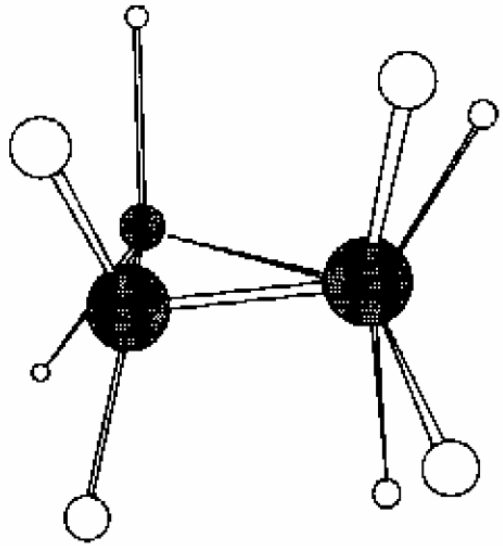


side-on view of planar cyclobutane shows eclipsing C–H bonds

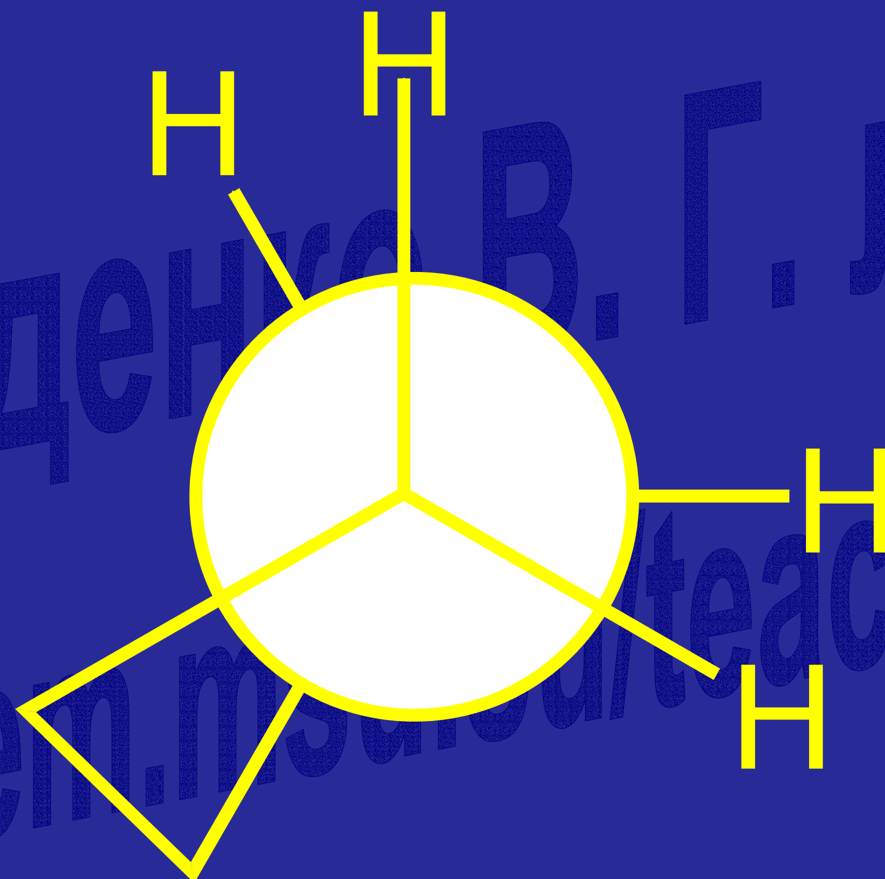


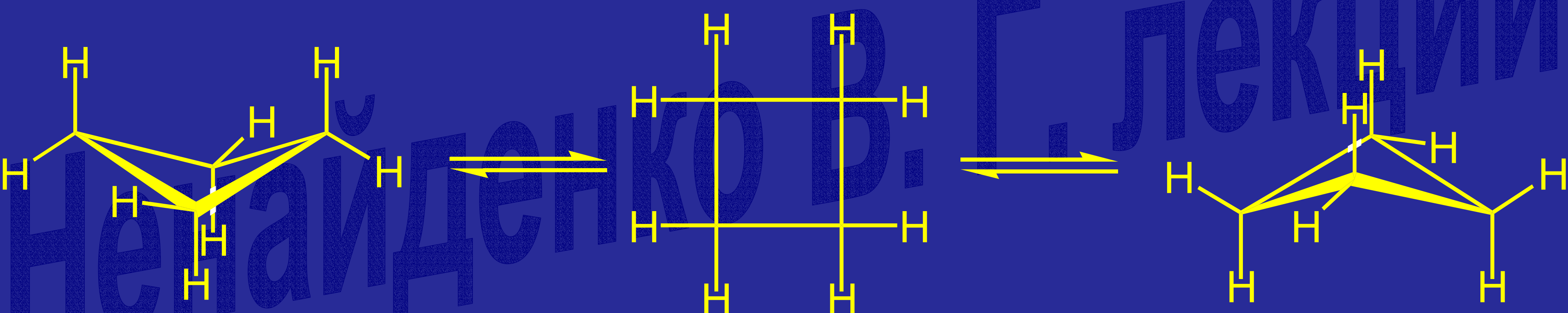
the puckered 'wing' conformation of cyclobutane

view along C–C

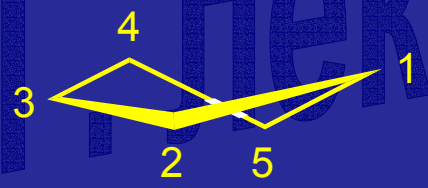


C–H bonds no longer fully eclipsed

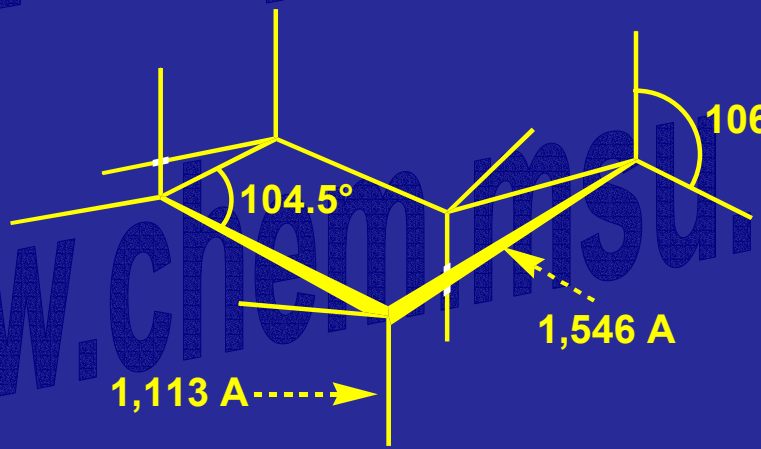


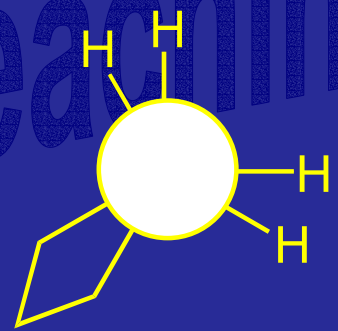


конверт

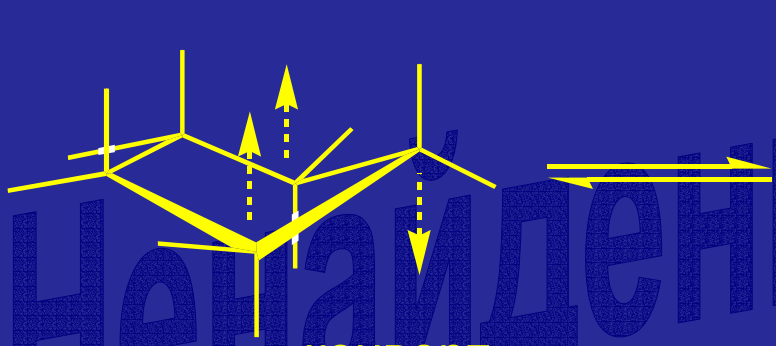


твист

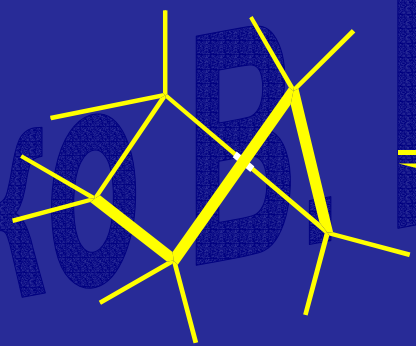




проекция Ньюмена

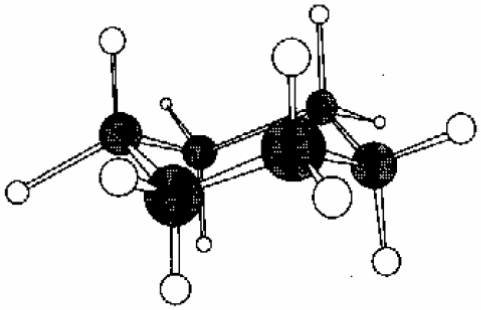


конверт

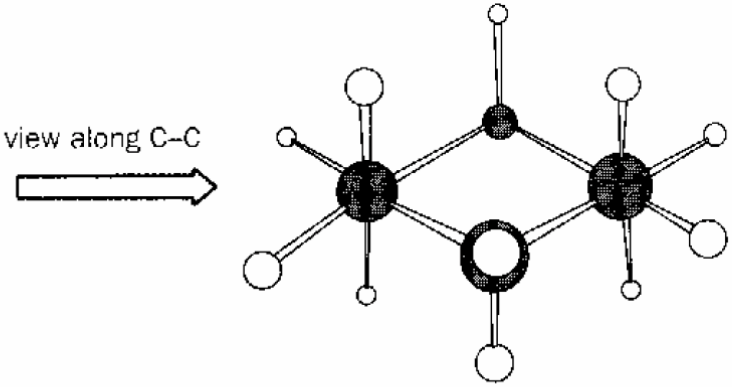


полукресло

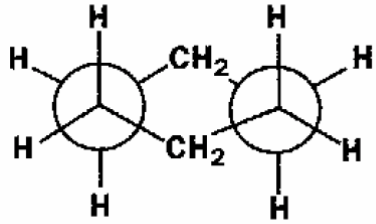
конверт



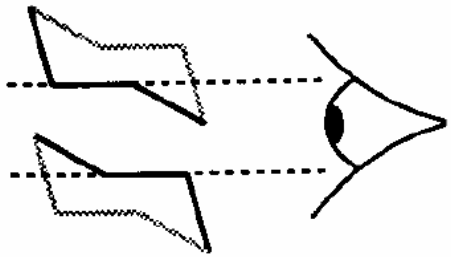
A side-on view of the chair conformation of cyclohexane

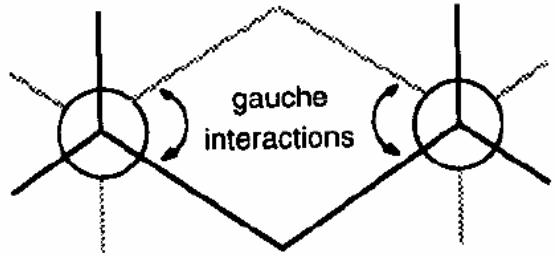


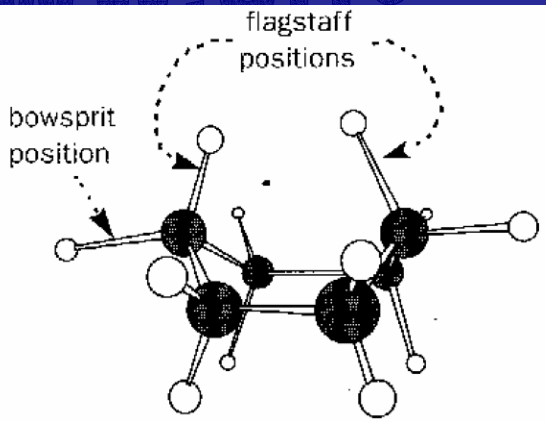
A view of cyclohexane looking along two of the C–C bonds.



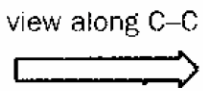
A Newman projection of the same view

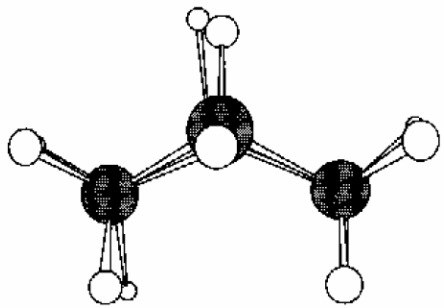




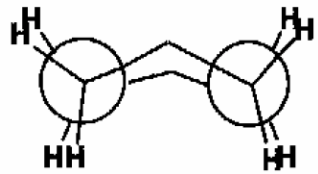


a side-on view of the boat conformation of cyclohexane

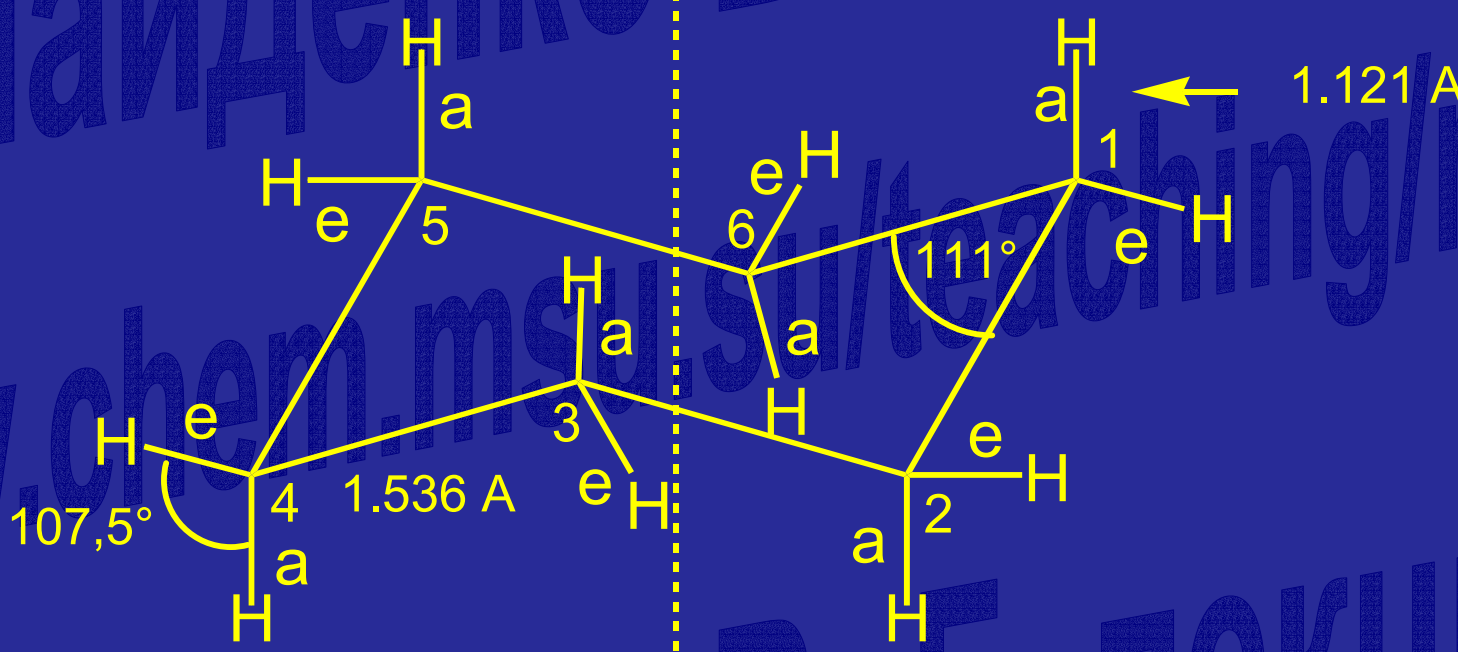


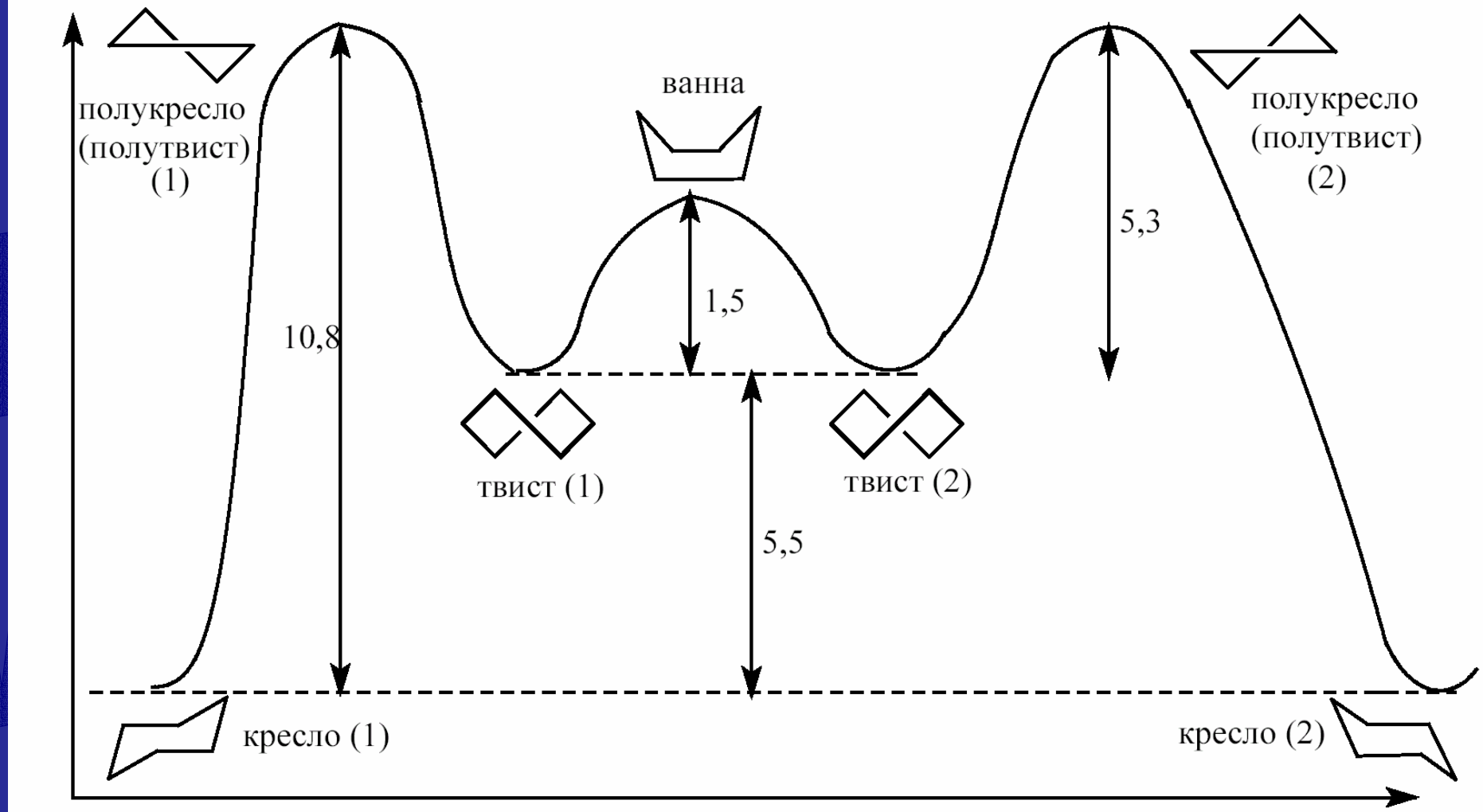


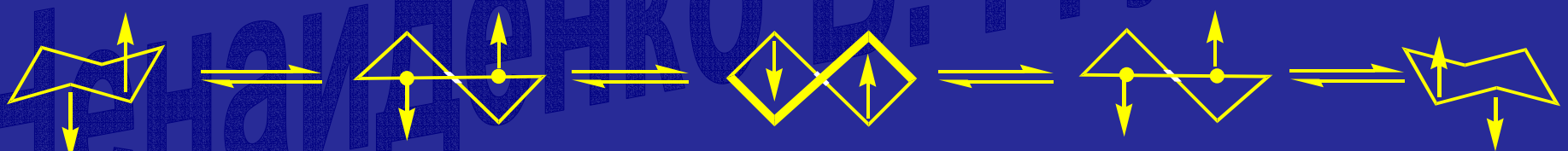
a view of the boat conformation looking along two of the C–C bonds

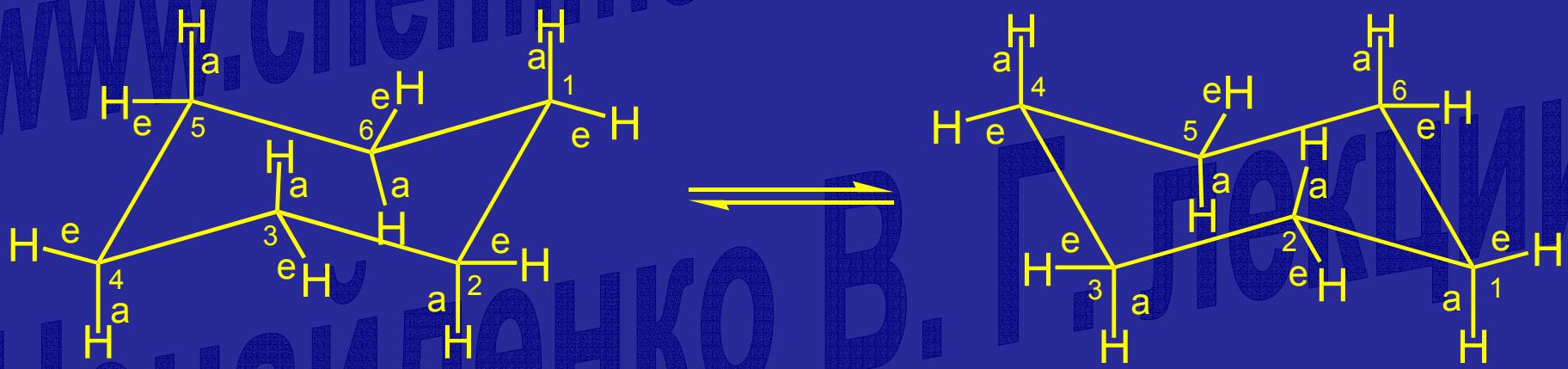


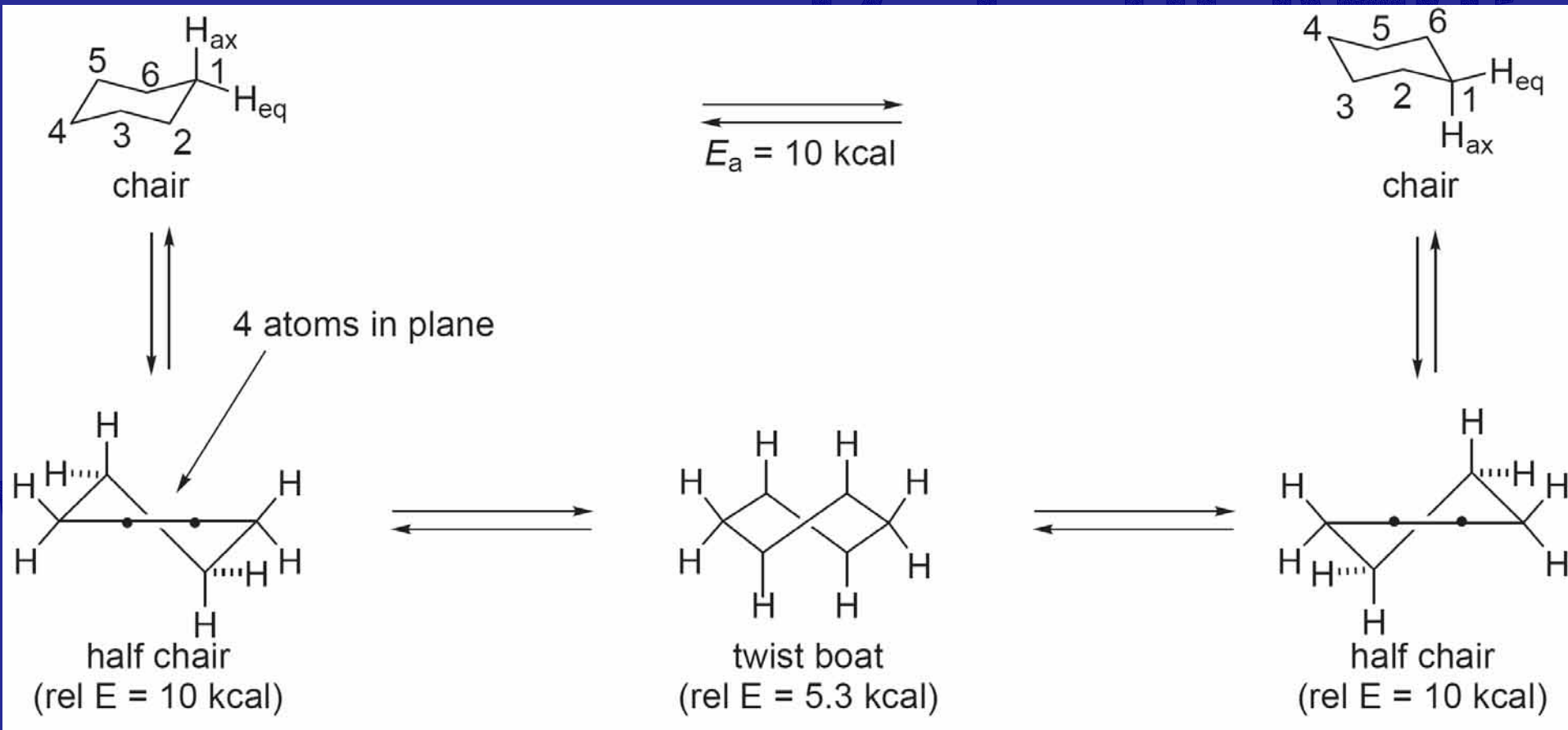
Newman projection of the same view



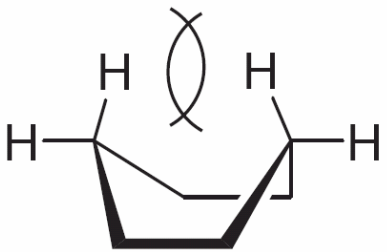

полукресло
(полутвист)
(1)
ванна
полукресло
(полутвист)
(2)
10,8
1,5
5,3
твист (1)
твист (2)
5,5
кресло (1)
кресло (2)






H_{ax}
H_{eq}
chair
E_a = 10 kcal
chair
4 atoms in plane
half chair
(rel E = 10 kcal)
twist boat
(rel E = 5.3 kcal)
half chair
(rel E = 10 kcal)

- Boat conformation



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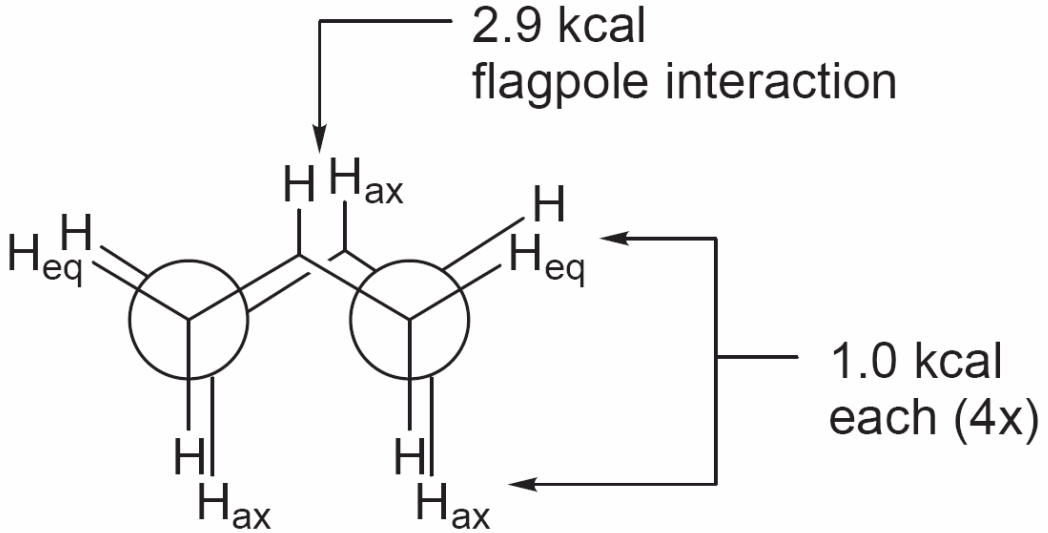
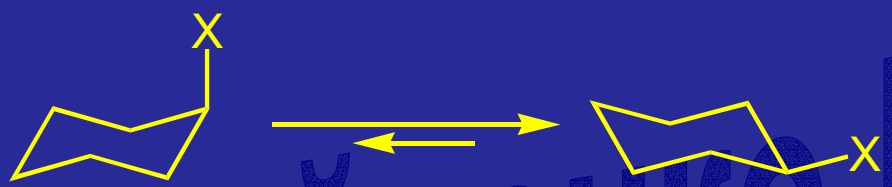
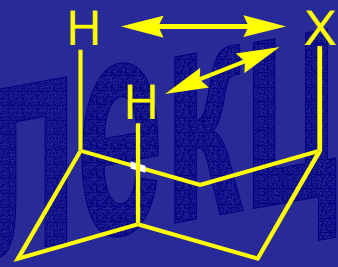


- Rel E = 6.9 kcal, not local minimum on energy surface.
- More stable boat can be obtained by twisting (relieves flagpole interaction somewhat).
- Twist boat conformation (rel E = 5.3 kcal) does represent an energy minimum.

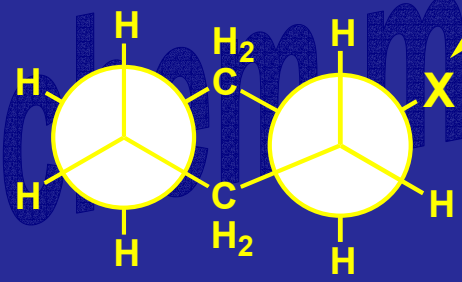




конформация с более низкой энергией

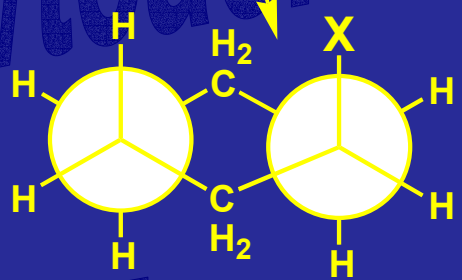
экваториально замещённый циклогексан

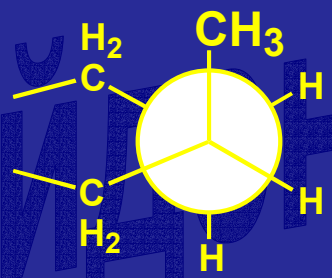
нет стерических затруднений



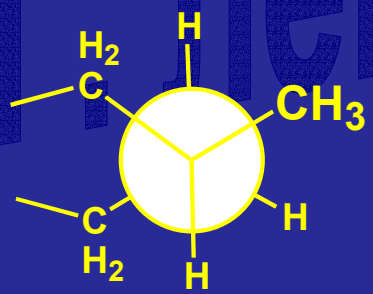
аксиально замещённый циклогексан

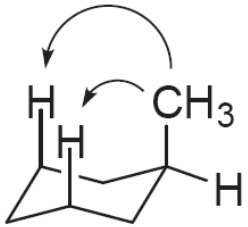
стерические затруднения

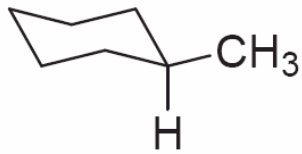




поворот на 60 °







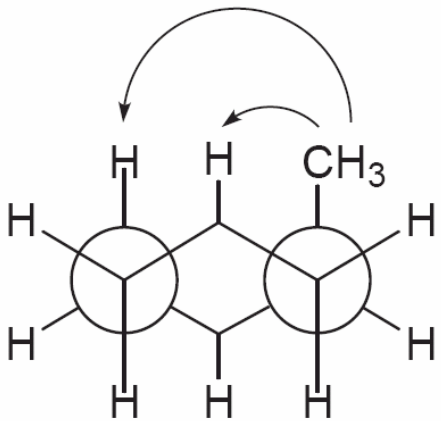
1.8 kcal more stable

$$\Delta G^\circ = -RT(\ln K)$$

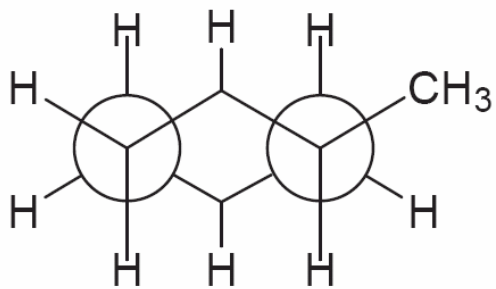
$$\frac{-1.8 \times 1000}{1.99 \times 298} = -\ln K$$

$$K = 21$$

- The gauche butane interaction is most often identifiable as 1,3-diaxial interactions.

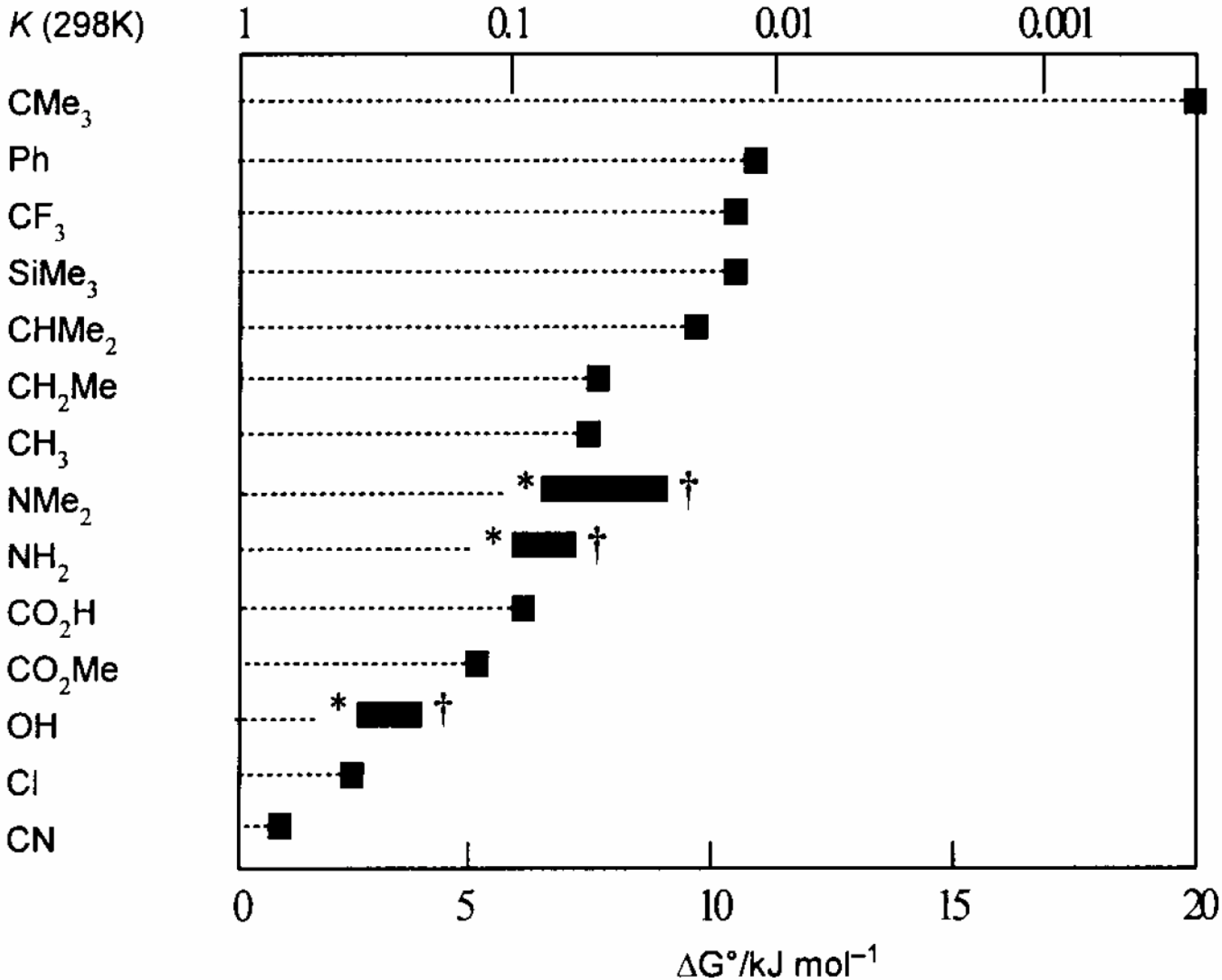


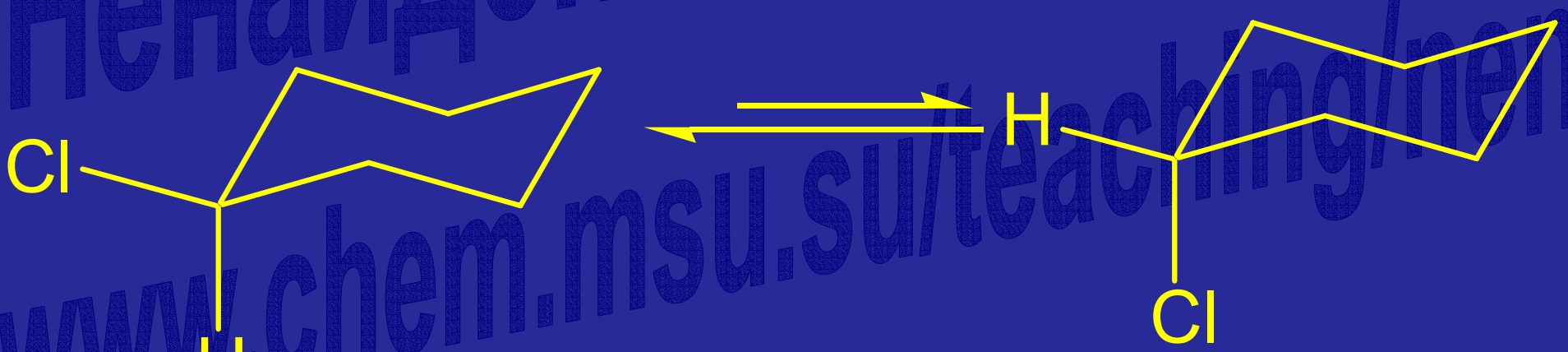
2 gauche butane interactions
2×0.9 kcal = 1.8 kcal
(experimental 1.8 kcal)



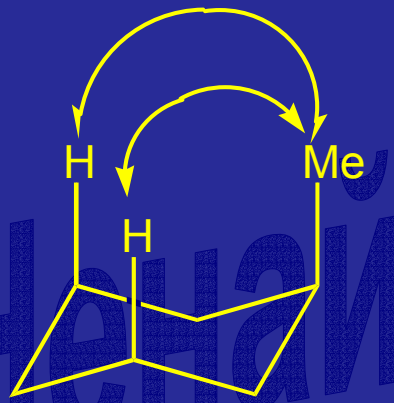
0 gauche butane interactions

Заместитель	Конформационная энергия ккал/моль
F	0.25
Cl	0.53
Br	0.48
I	0.47
Me	1.8
Et	1.8
i-Pr	2.1
t-Bu	5.4
Ph	3.1
CN	0.15-0.25
COOH	1.35
OH (протон)	0.87
OH (апротон)	0.52
OMe	0.60
NO_2	1.16

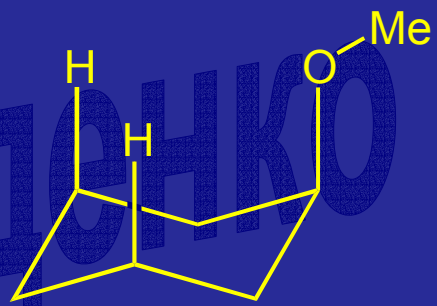

K (298K)
1
0.1
0.01
0.001
CMe3
Ph
CF3
SiMe3
CHMe2
CH2Me
CH3
NMe2
NH2
CO2H
CO2Me
OH
Cl
CN
0
5
10
15
20
ΔG°/kJ mol−1



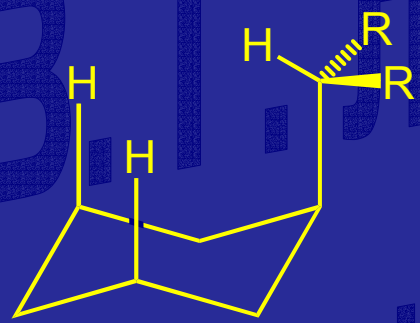
$t_{1/2}$ = 22 года при -160 ^{o}C



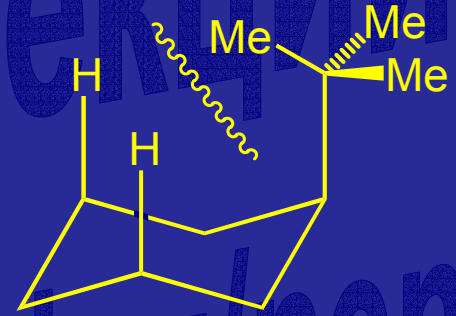
1,3-взаимодействие между метильной группой и аксиальными водородами



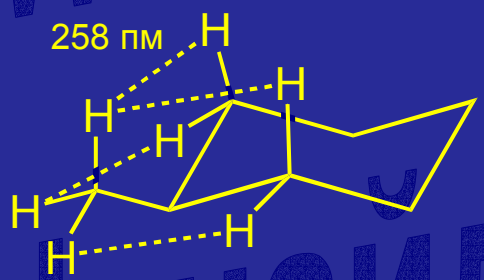
В метоксициклогексане метильная группа удалена из зоны кольца



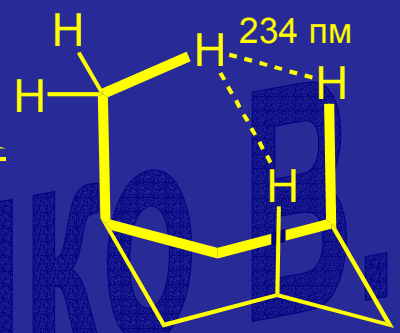
1,3-взаимодействие с Me, Et, i-Pr



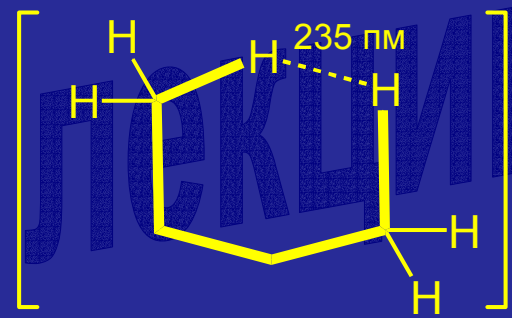
В *t*-Bu-циклогексане существуют сильные стерические взаимодействия в аксиальном конформере



e-метилциклогексан



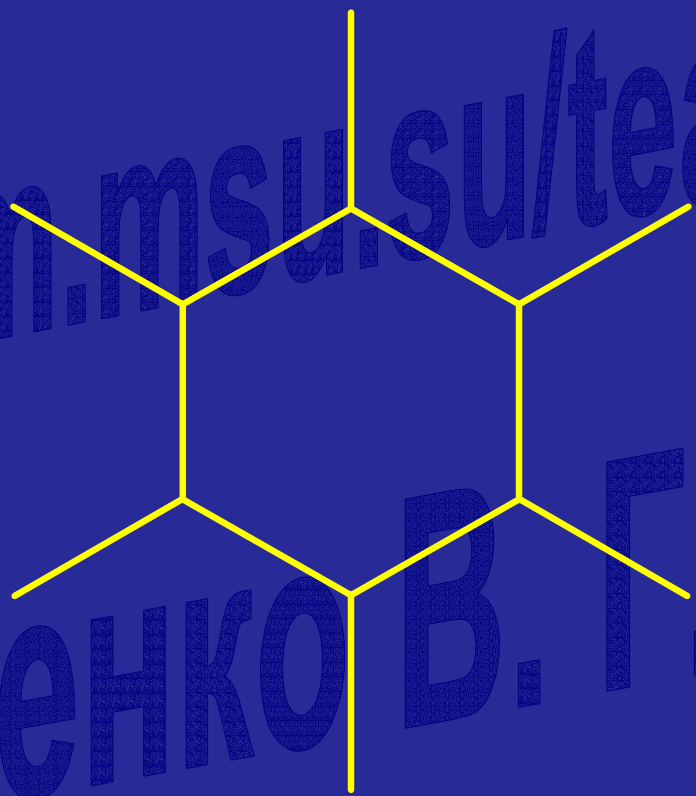
a-метилциклогексан

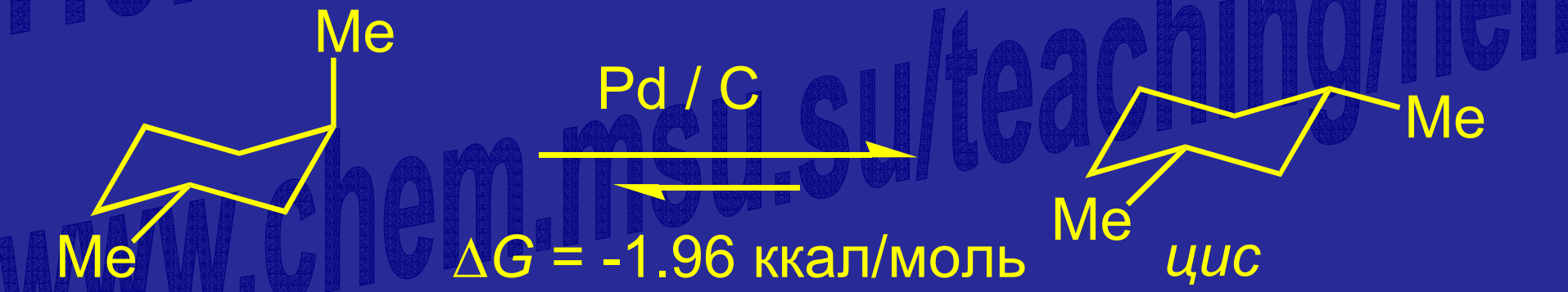


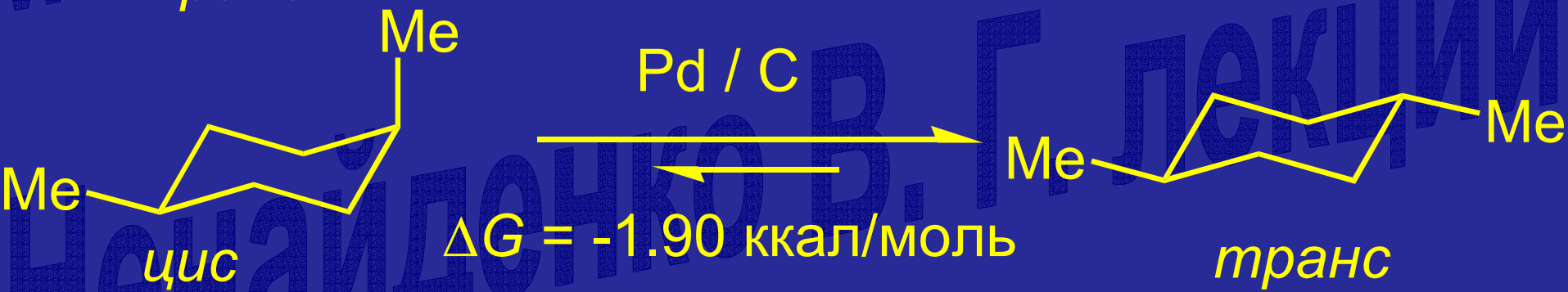
сравните с *гош*-взаимодействием в *н*-бутане

Задание на дом

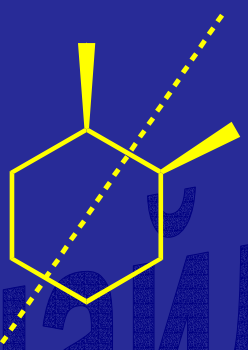
Нарисуйте все изомеры, какой из них будет самым устойчивым





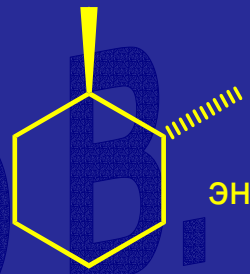


1,2-Диметилциклогексан

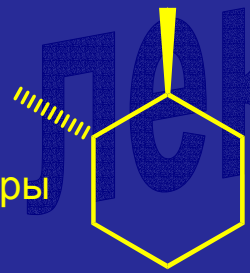


цис

диастереомеры



энантиомеры



транс

1,3-Диметилциклогексан

цис

диастереомеры

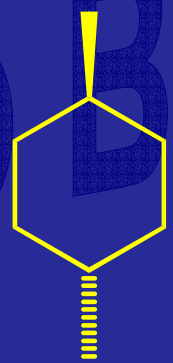
энантиомеры

транс

1,4-Диметилциклогексан

цис

диастереомеры



транс