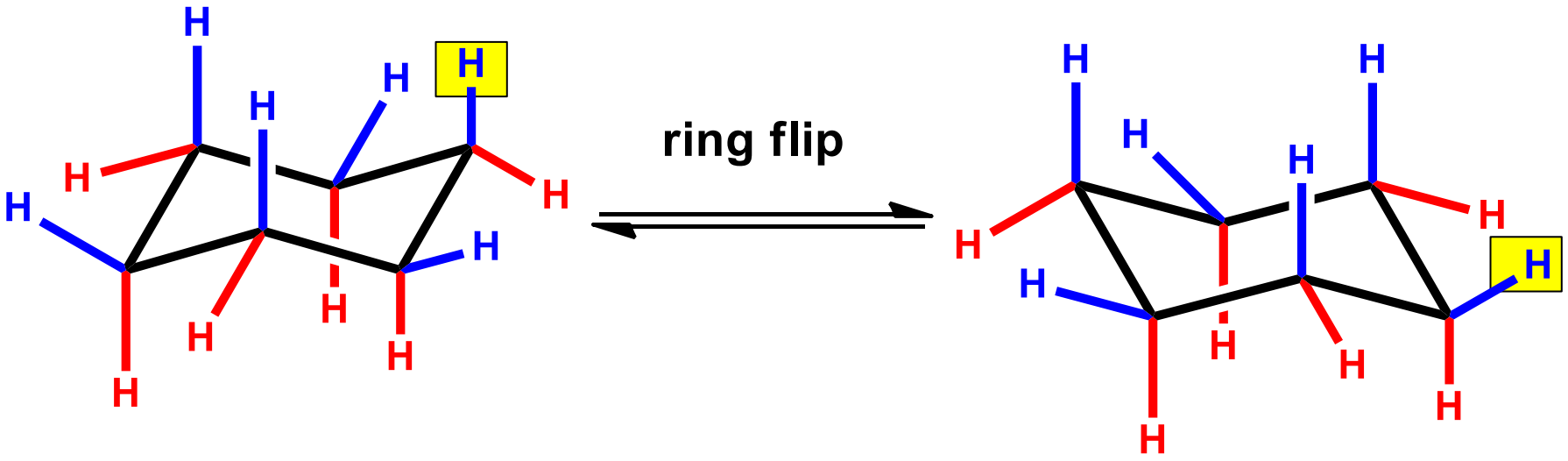
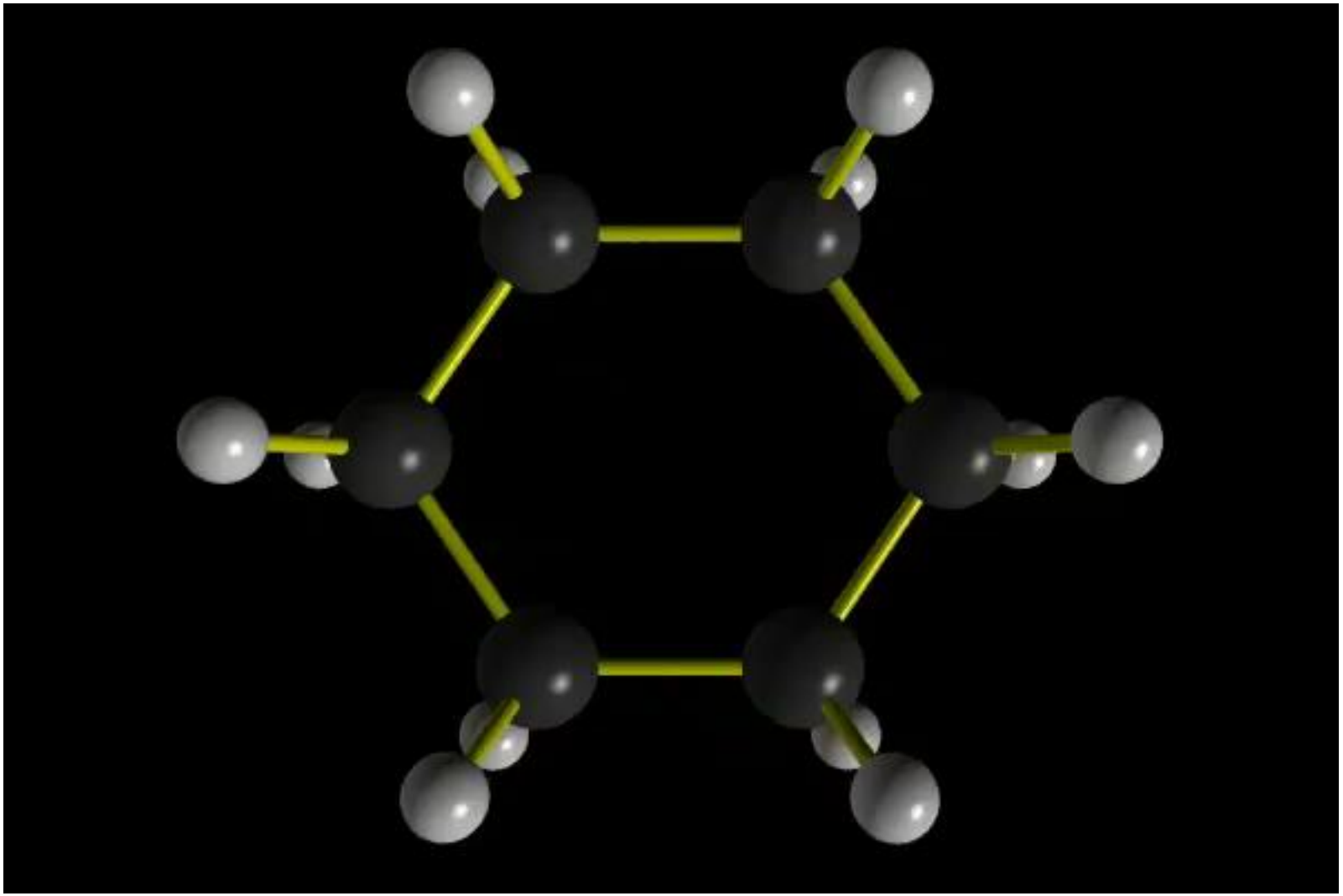
The Ring Flip Causes Equatorial-Axial Exchange



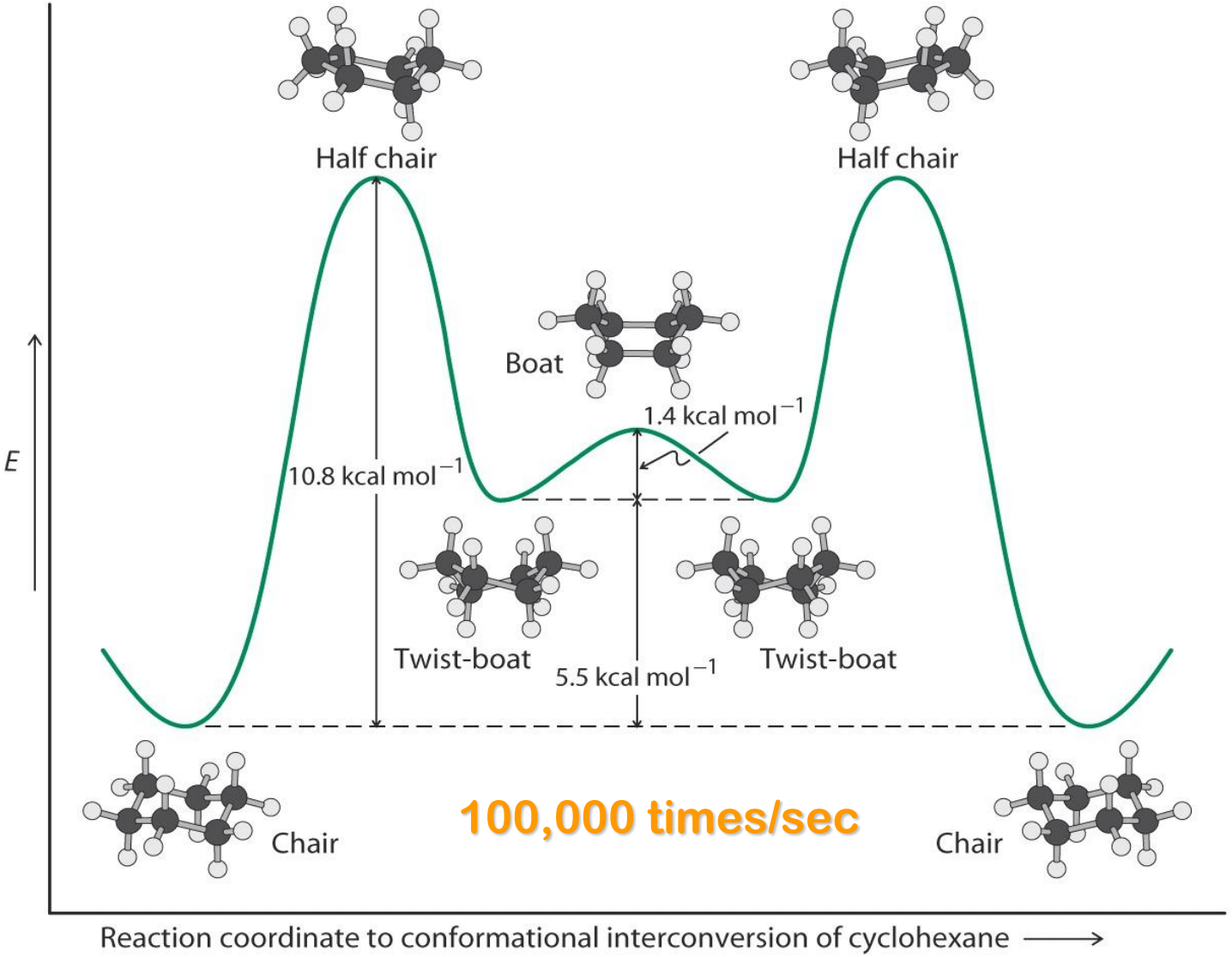
The two structures are the same!

Ring Flip



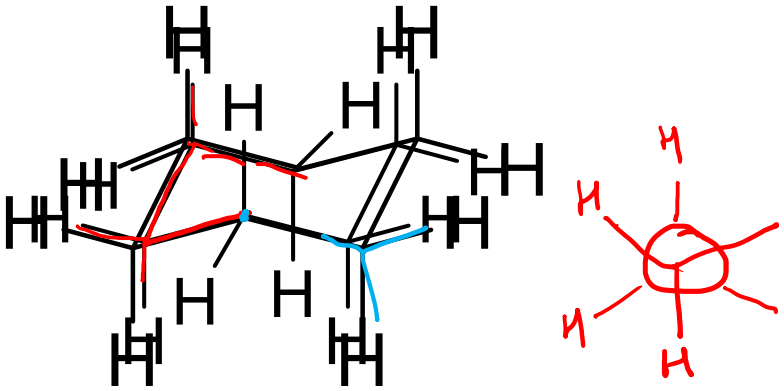
Ring Flipping - Energetics

In monosubstituted (small groups) cyclohexanes the ring flipping is of the order of 10^4 to 10^5 inversions/second

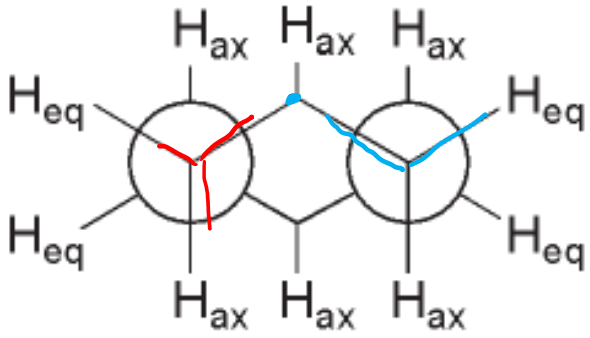


Chair v/s Boat : Newman Projection

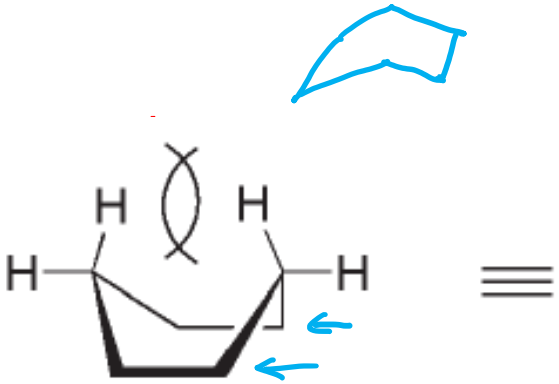
Chair



Staggered form

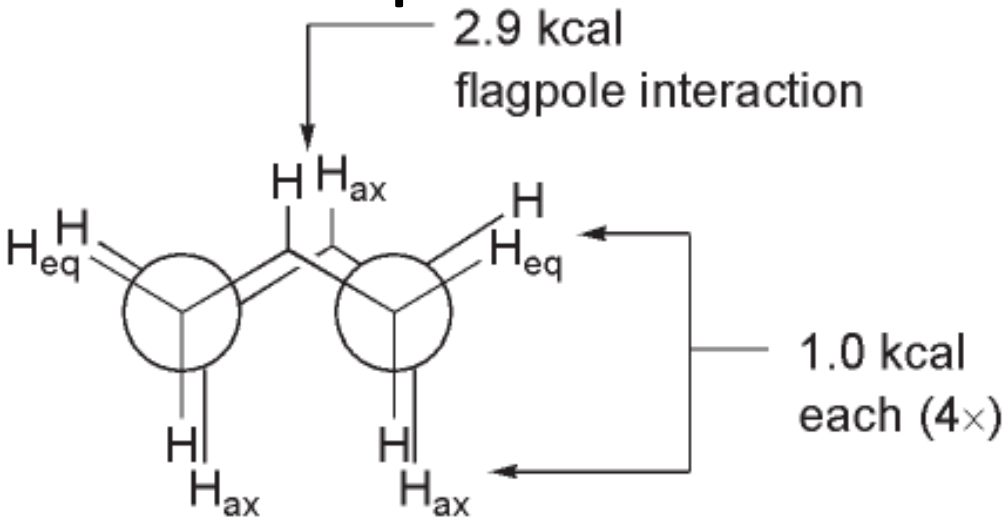


Boat



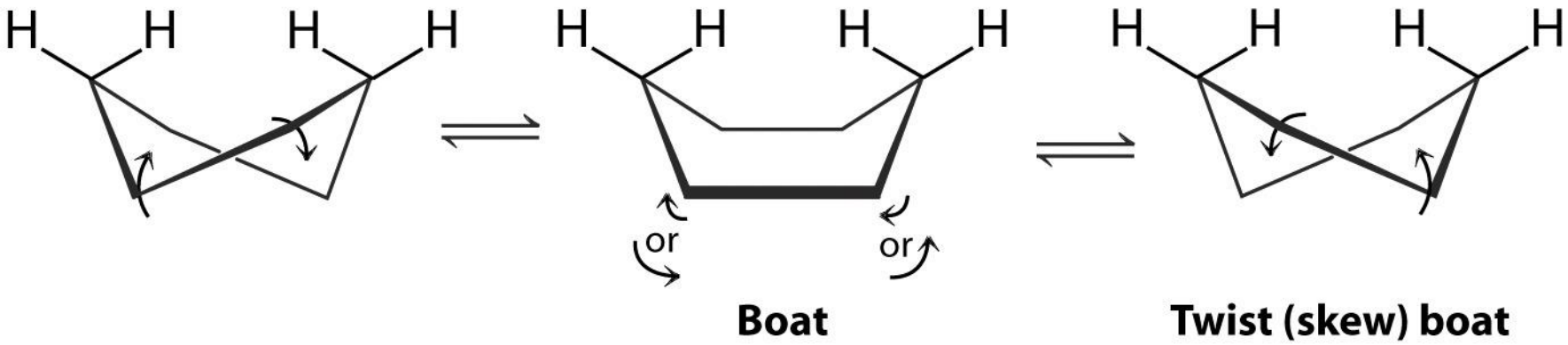
≡

Eclipsed form



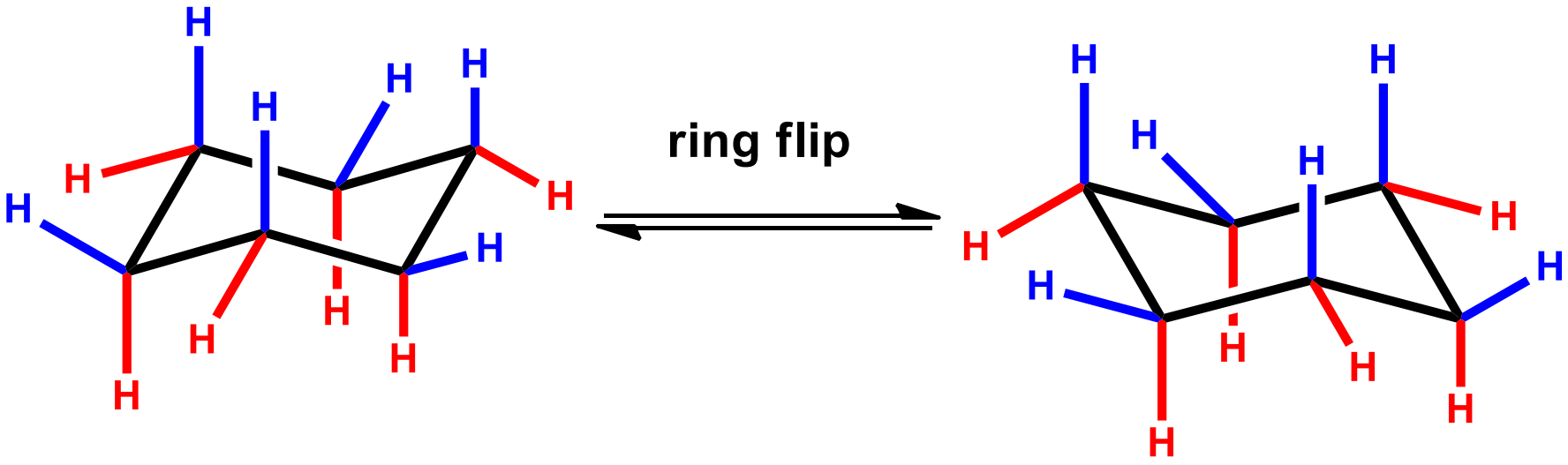
Rel E = 6.9 kcal

Relief by Twisting



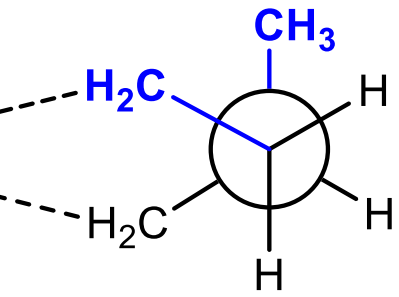
But this is only part of its mobility. The molecule "flips" from one chair to another chair form.

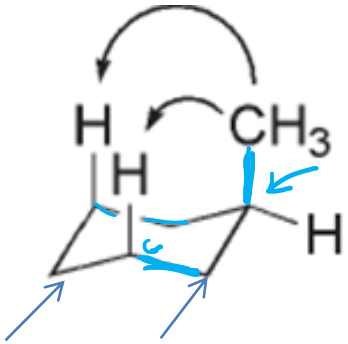
Ring Flip - Summary



The two structures are the same.
What happens in substituted cyclohexanes?

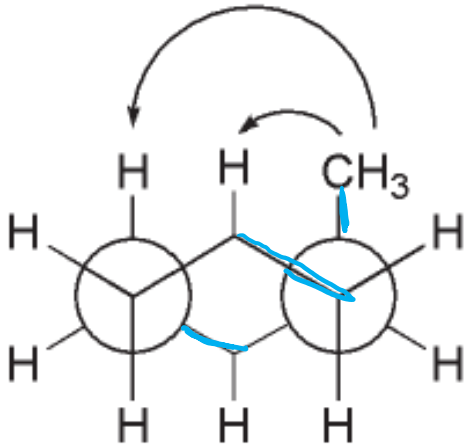
Methylcyclohexane





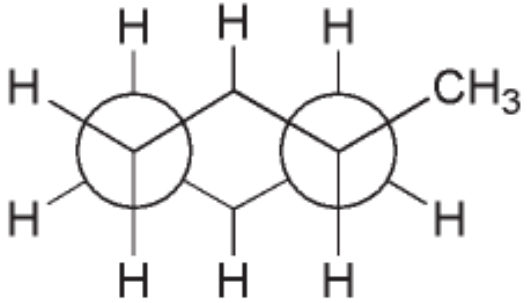
View

1.8 kcal more stable



2 gauche butane interactions

2×0.9 kcal = 1.8 kcal



0 gauche butane interactions

1,3-Diaxial interactions are just gauche butane interactions

A-Values

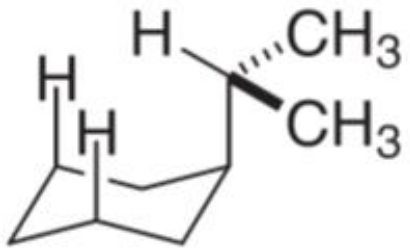
Free energy difference between equatorial and axial conformer

Typical A Values

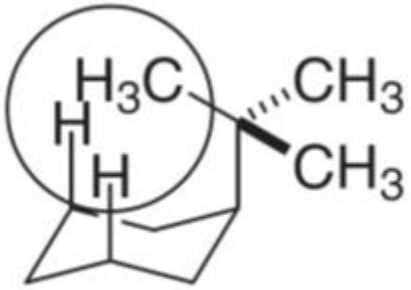
R	A Value (kcal/mol)		R	A Value (kcal/mol)	
F	0.25	Size vs bond length ↓	CHO	0.6–0.8	
Cl	0.52	ca. 0.5 kcal	$COCH_3$	1.2	
Br	0.5–0.6	ca. 0.5 kcal	CN	0.2	Small, linear groups
I	0.46	ca. 0.5 kcal	C≡CH	0.41	Small, linear groups
OH	0.7 (0.9)	ca. 0.7 kcal (2^{nd} atom effect very small)	NO_2	1.1	
OCH_3	0.75	ca. 0.7 kcal (2^{nd} atom effect very small)	$CH{=}CH_2$	1.7	
$OCOCH_3$	0.71	ca. 0.7 kcal (2^{nd} atom effect very small)	CH_3	1.8	2^{nd} atom effect very small
NH_2	1.8 (1.4)		CH_2CH_3	1.9 (1.8)	2^{nd} atom effect very small
NR_2	2.1		$^nC_3H_7$	2.1	2^{nd} atom effect very small
CO_2H	1.2 (1.4)		$^nC_4H_9$	2.1	2^{nd} atom effect very small
CO_2Na	2.3		$CH(CH_3)_2$	2.1	2^{nd} atom effect very small
CO_2Et	1.1		$C(CH_3)_3$	>4.5 (ca. 5.4)	
SO_2Ph	2.5		C_6H_5	3.1 (2.9)	

A-Values Difference

- Note on difference between ^{i}Pr and ^{t}Bu A values.



^{i}Pr group can position H toward "inside,"

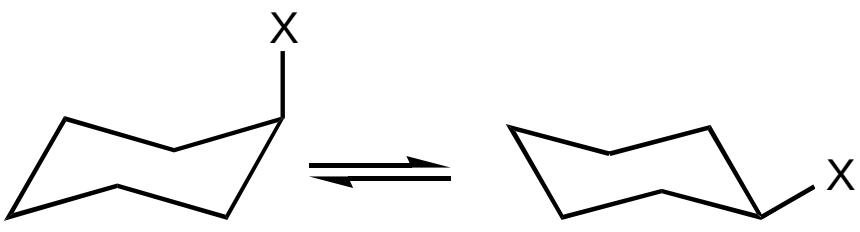


but ^{t}Bu group cannot.
Very serious interaction, 7.2 kcal.

Homework – Derive how A value of *t*-butyl is 5.4 kcal

A-Values and Equilibrium Constant

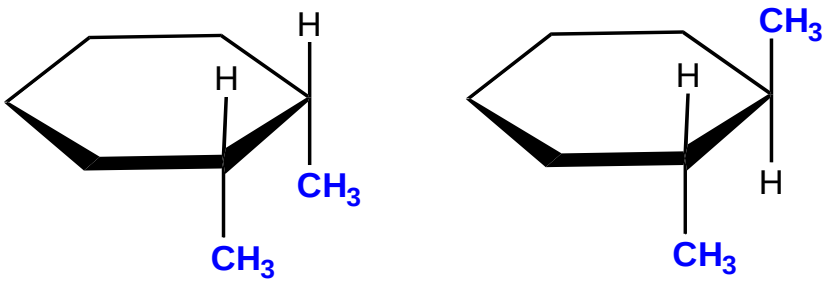
$$\Delta G = G_{ax} - G_{eq}$$



X group	A value (kcal/mol)	K	% eq
H	0	1	50
CH_3	1.7	19	95
$CH(CH_3)_2$	2.15	42	98
$C(CH_3)_3$	5	3000	99.9

Disubstituted Cyclohexanes

1,2-disubstituted

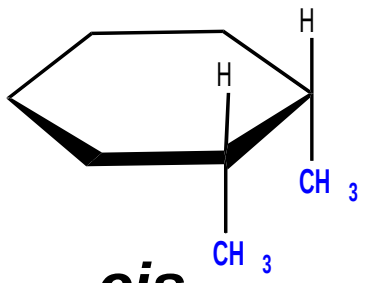


cis ***trans***

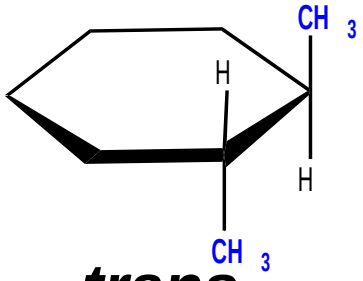
Draw the chair form for these molecules and do the ring flip

Disubstituted cyclohexanes

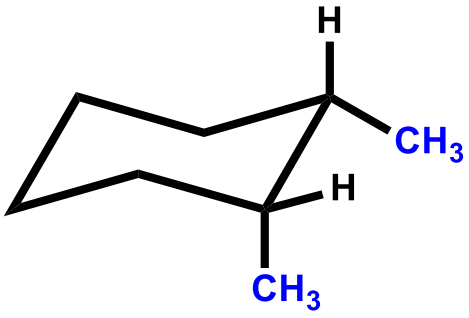
1,2-disubstituted



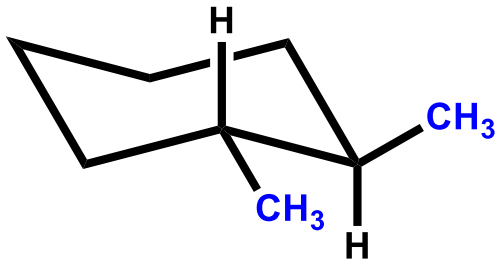
cis



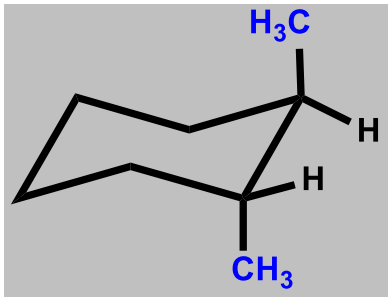
trans



cis



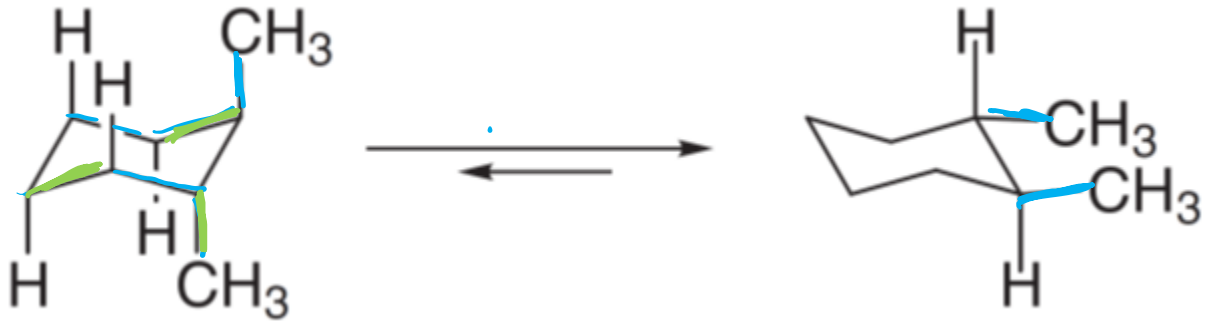
trans



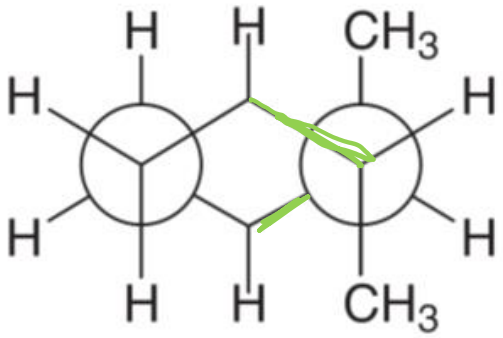
trans

Can we calculate the energy difference?

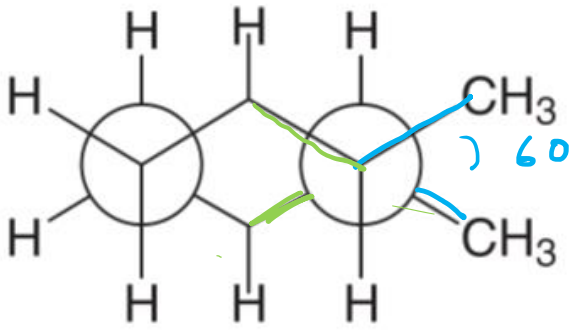
trans-1,2-Dimethylcyclohexane



2.7 kcal/mol more stable



4 × (gauche interaction)
4 × (0.9 kcal) = 3.6 kcal

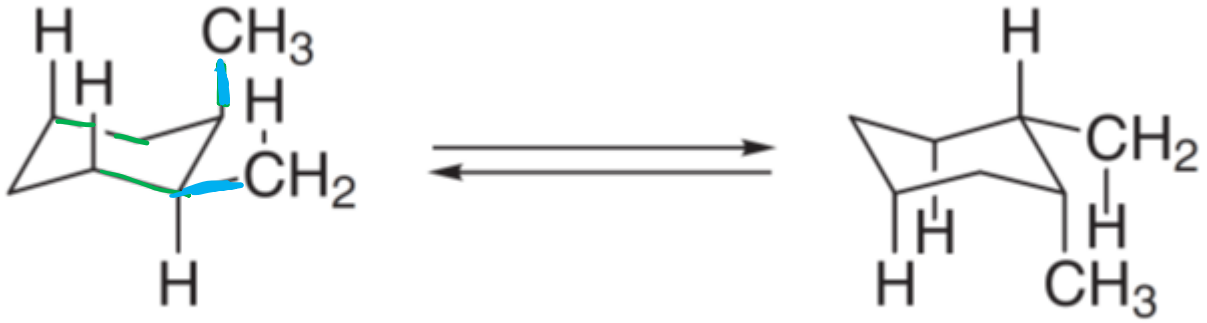


1 × (gauche interaction)
1 × (0.9 kcal) = 0.9 kcal

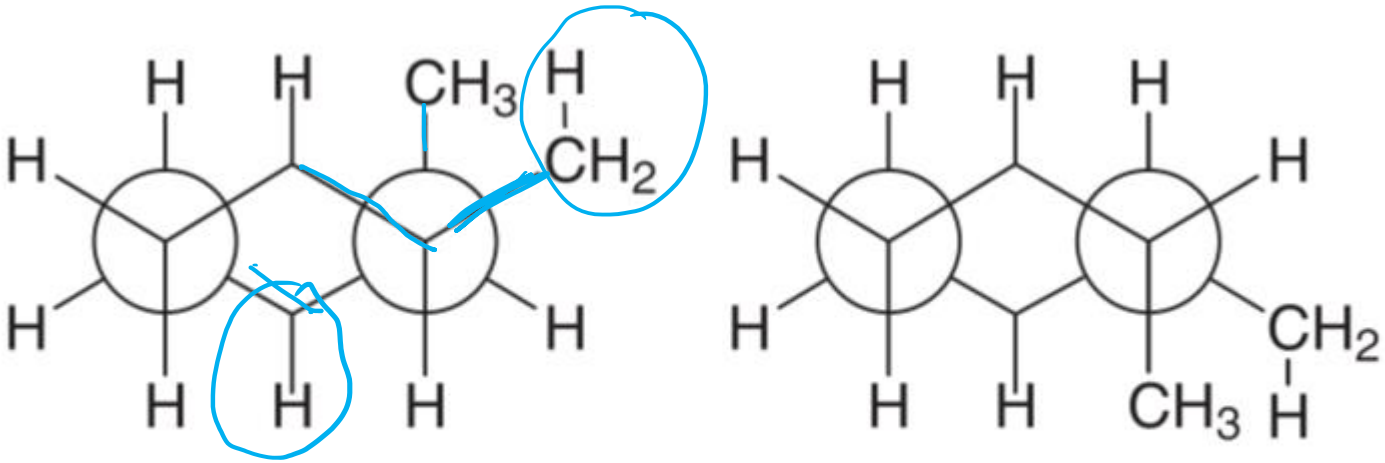
60°

Butane

cis-1,2-Dimethylcyclohexane



$\Delta E = 0$ kcal/mol



3 × (gauche interaction)
3 × (0.9 kcal) = 2.7 kcal

3 × (gauche interaction)
3 × (0.9 kcal) = 2.7 kcal

Homework: Analysis for *cis* and *trans*-1,3-dimethylcyclohexane