Equatorial preference (A-factor) for different groups:

CH_3	1.84
F	0.15
isopropyl	2.21
t-Butyl	5.4

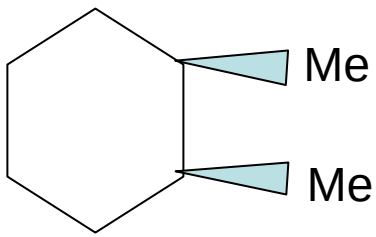
→ 99% equatorial

It means that other subst. are also “frozen” in place

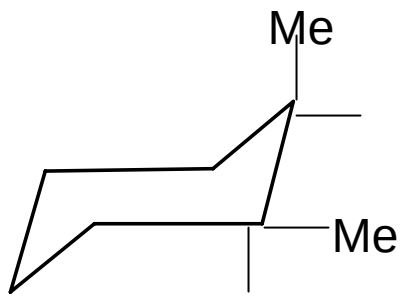
If two subst. on the ring, A-values are usually additive
-unless there is interaction b/w subst.

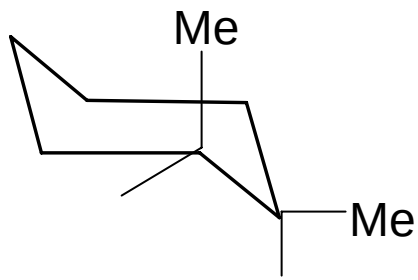
1,2-dimethylcyclohexane

Cis-



Two 1,3-diaxial interactions + gauche between 2 Me



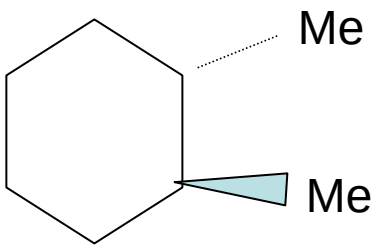


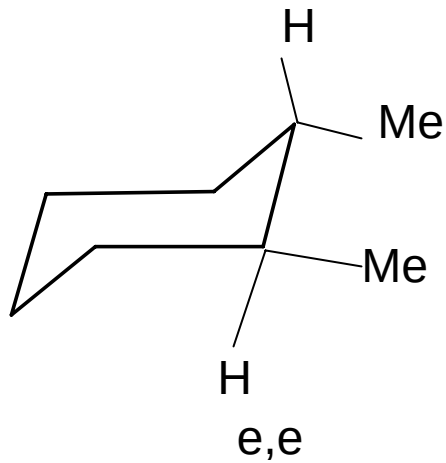
e,a

a, e

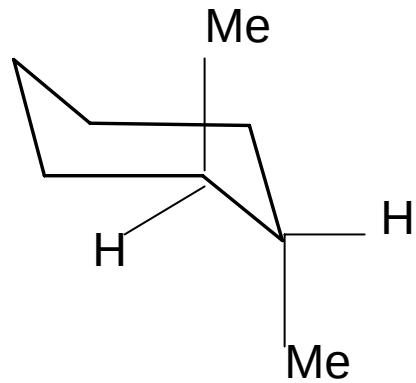
50% : 50%

trans-





e,e



a,a

No 1,3-diaxial,
one gauche- b/w Me

Lowest E

4 1,3-diaxial interactions (3.6)

Compare cis- and trans-

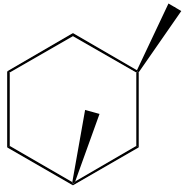
a,e e,e

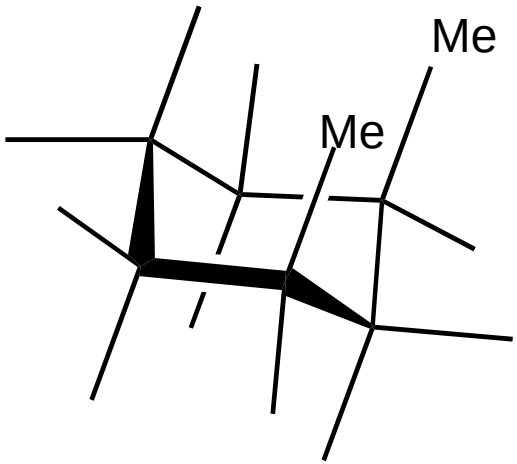
Two more interactions than trans-

0.9 x 2=1.8 kcal/mol

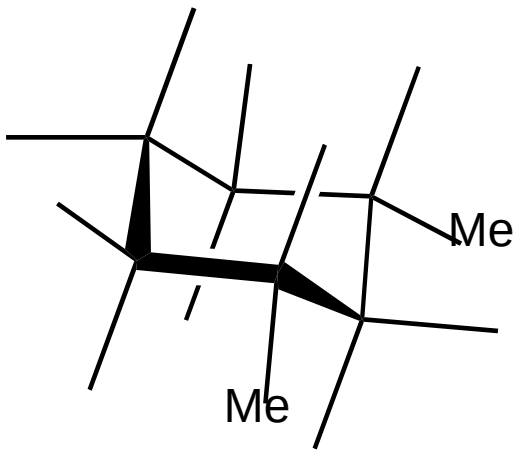
1,3-dimethylcyclohexane. No gauche, only 1,3 diaxial interaction

cis-



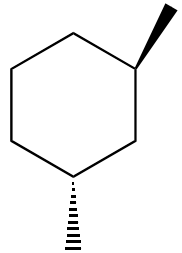


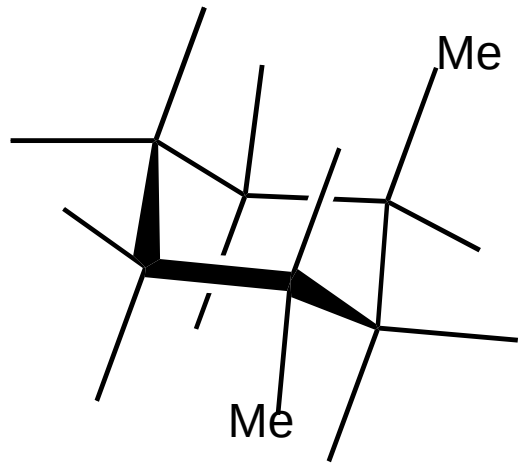
a,a



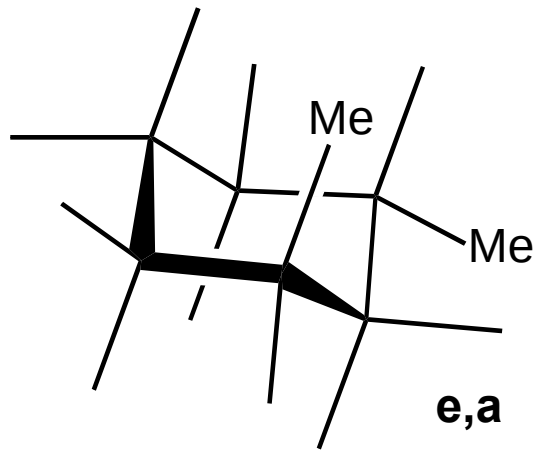
e,e

trans-





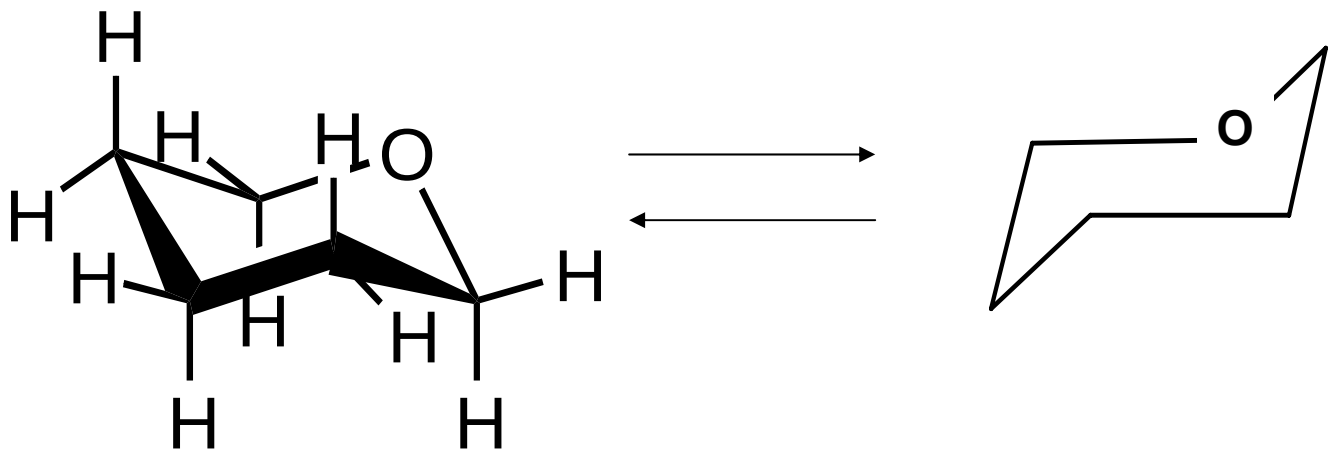
a,e

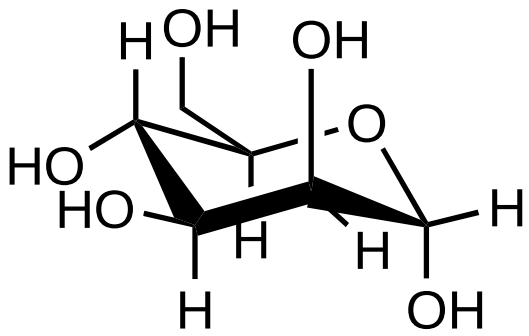


e,a

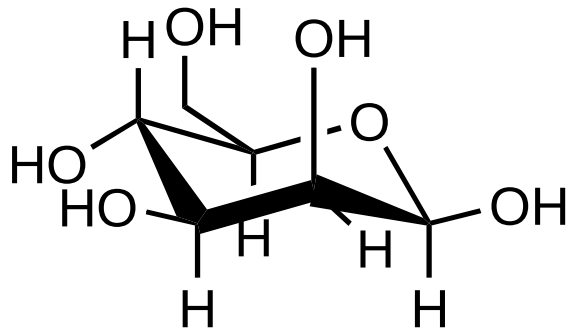
Tetrahydropyran

The preferred conformation of the tetrahydropyran ring is the chair conformation.





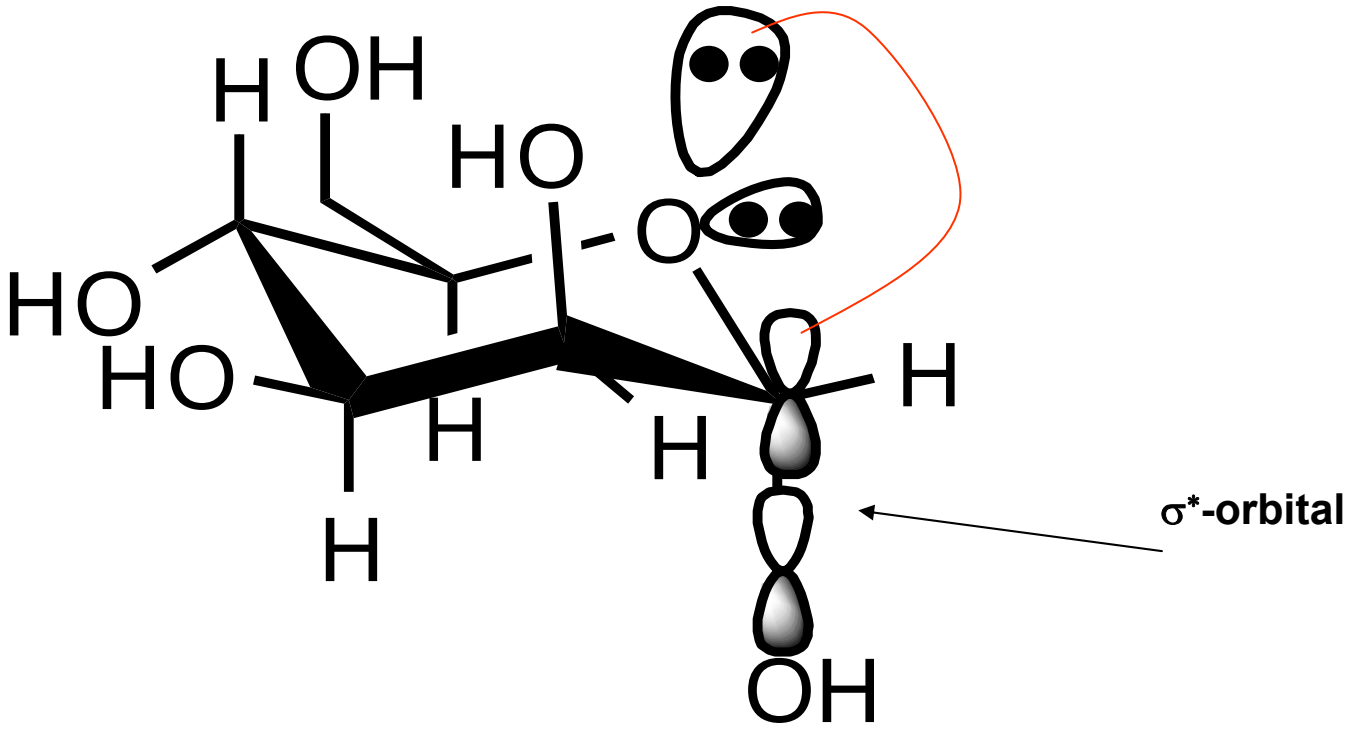
α-D-mannose



β-D-mannose

Anomeric effect: states that electronegative substituents at the anomeric center of pyranoses prefer to adopt an axial configuration.

one of the lone pairs on oxygen overlaps with the antibonding σ^*-orbital of the C-O bond. The overlap is efficient only when one of the electron lone pairs on the oxygen is antiperiplanar with the C-O bond.

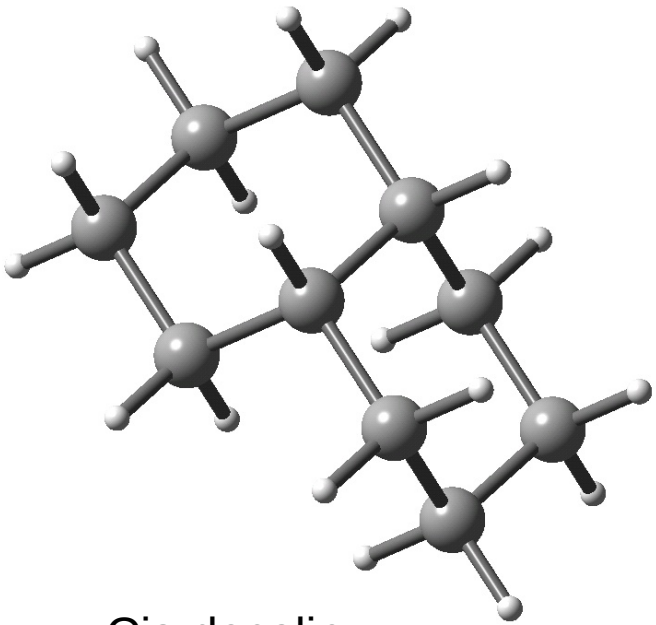


Anomeric effect cancels bond dipoles. Better seen in nonpolar solvents

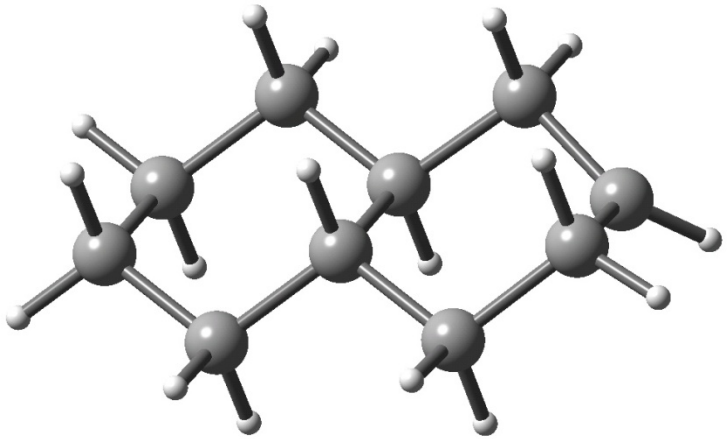
Ring fusion - steroids

“lock” cyclohexane in particular chair conformation by fusion a second ring onto it

2 ways: cis (two H atoms are cis) and trans (two H atoms are trans)



Cis-decalin



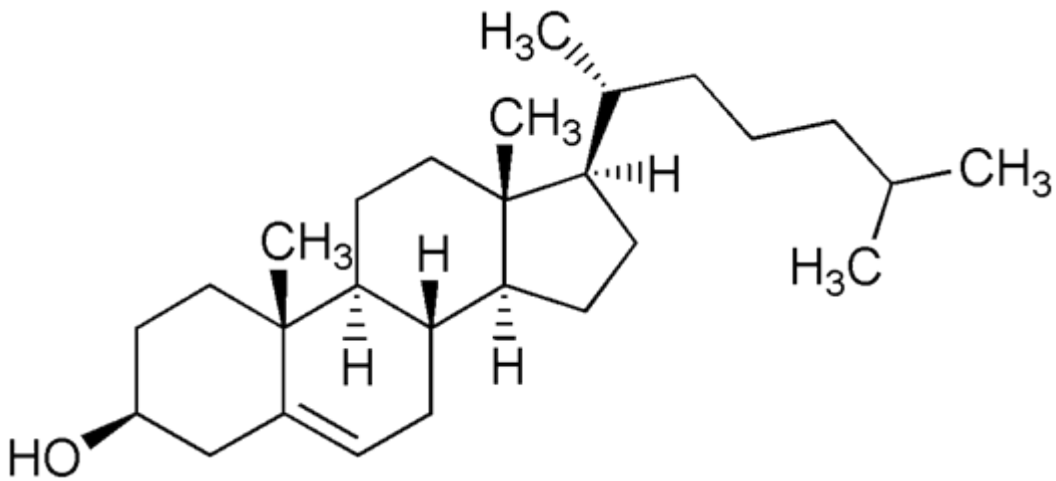
trans-decalin

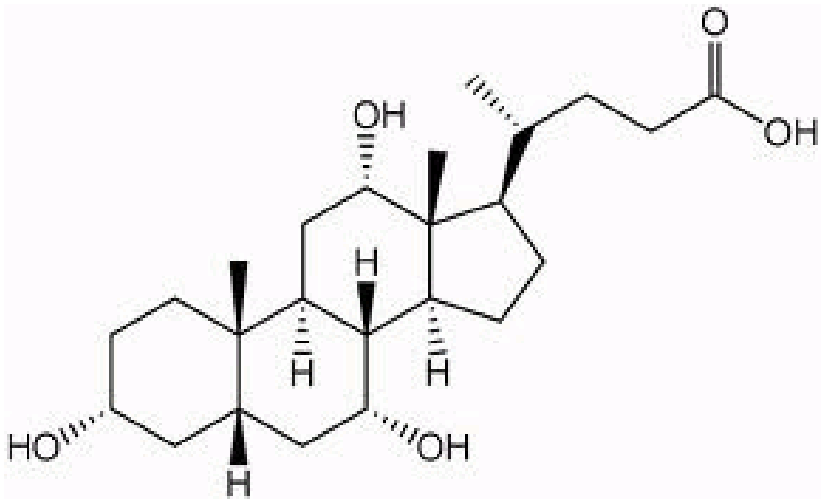
Cis- is flexible as the axial and equatorial can interconvert (chair flapping process)

Trans- not interconvertable. 3 kcal/mol lower than cis. Disk-like structure- rigid – typical of steroids

Most steroids (e.g. cholesterol, testosterone) are trans- (rigid, dislike).

Biological function of cholesterol – inserts into cell membrane and stabilizes it





Cholic acid: one cis and one trans-fusion. Gives flexibility and creates juxta-position for the 3 OH-groups (always opposite and parallel to each other

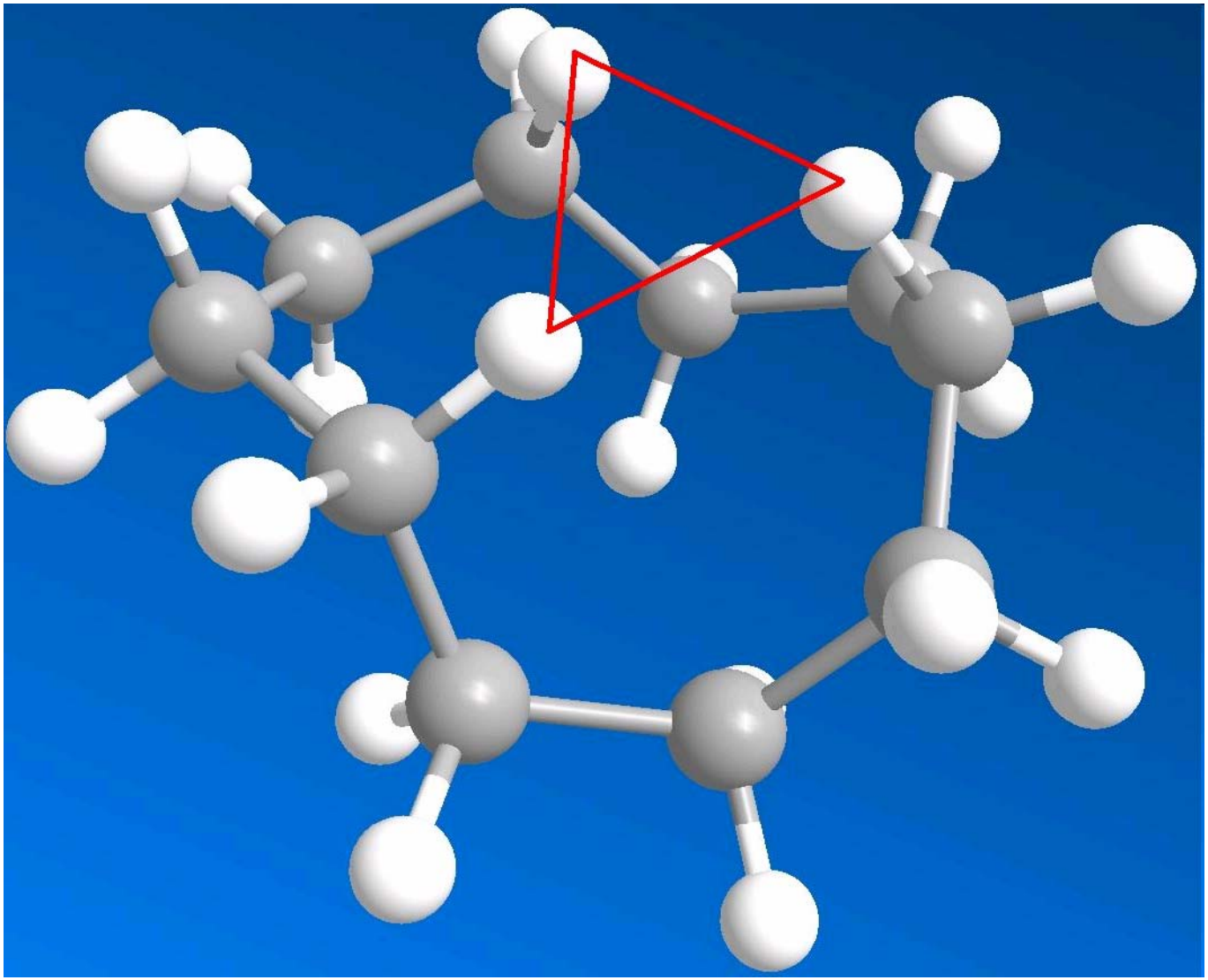
Strain energy (kcal/mol) in cycloalkanes $(CH_2)_n$:

n	3	4	5	6	7	8	9	10	11
Strain Energy	27.5	26.3	6.2	0.1	6.2	9.7	12.6	12.4	11.3

n	12	13	14	15	16
Strain Energy	4.1	5.2	1.9	1.9	2.0

Why the strain energy increases with n>6 and decreases again with n>13?

Trans-annular strain



Trans-annular strain in cyclodecane