biolab

COMPOSTOS ORGÂNICOS: ALCANOS E CICLOALCANOS

ANÁLISE CONFORMACIONAL

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ÍNDICE

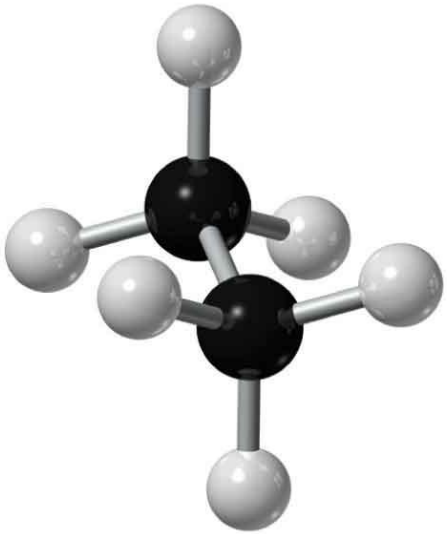
ANÁLISE CONFORMACIONAL

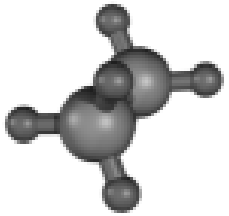
- Estruturas resultantes de uma símples rotação em torno de uma ligação símples C-C.

- Podem apresentar diferentes energias. A estrutura (conformação) de menor energia é a mais estável.

- Moléculas estão constantemente girando e passando através de diferentes confôrmeros.

ANÁLISE CONFORMACIONAL

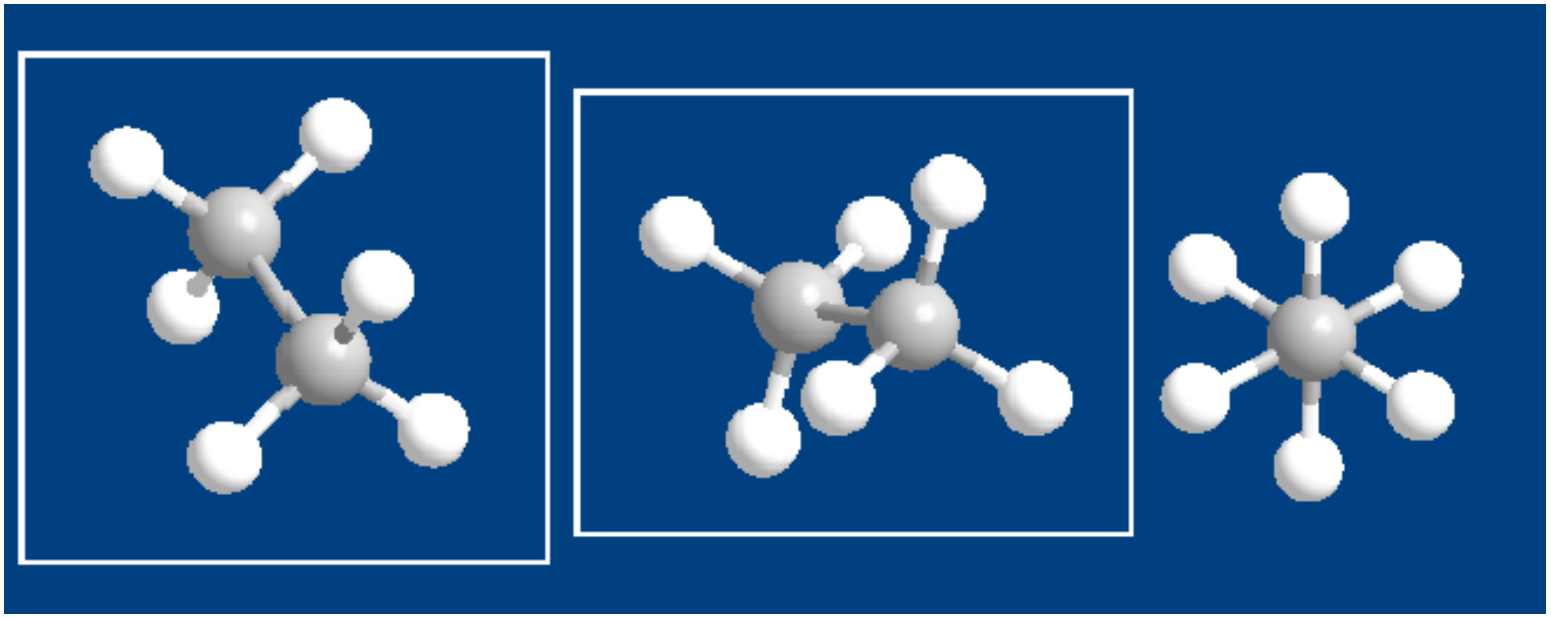




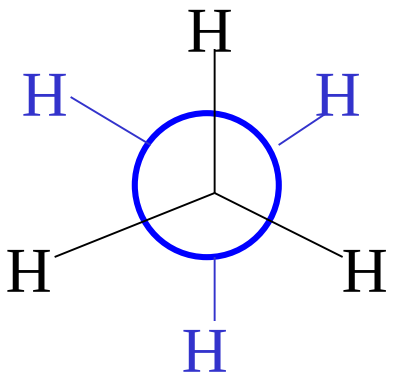
INFLUÊNCIA NA ESTABILIDADE: FATOR ESTÉRICO (PROXIMIDADE DE GRUPOS).

QUANTO MAIOR A DISTÂNCIA ENTRE GRUPAMENTOS VOLUMOSOS, MENOR O IMPEDIMENTO E A INTERAÇÃO ESTÉRICA E MAIOR É A ESTABILIDADE.

ANÁLISE CONFORMACIONAL: PROJEÇÃO DE NEWMAN

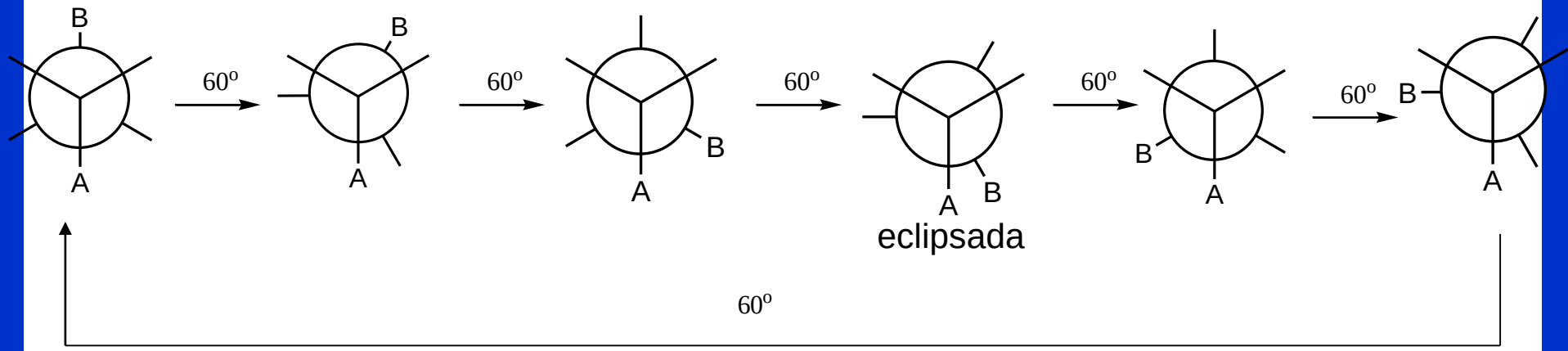


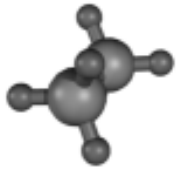
Projeção de Newman



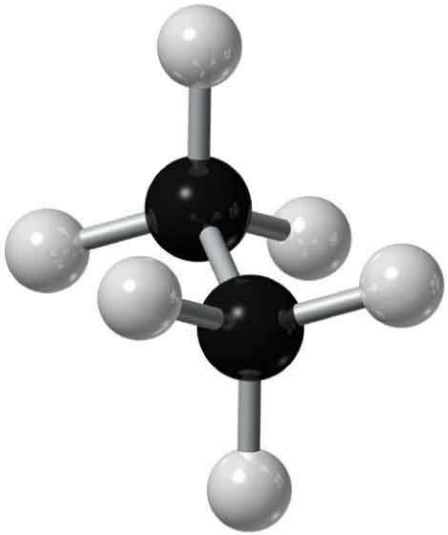
ANÁLISE CONFORMACIONAL: CONFÔRMEROS

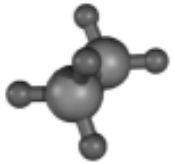
- PARA A FORMAÇÃO DOS CONFÔRMEROS DEIXA-SE FIXO UM DOS CARBONOS E GIRA-SE O OUTRO EM ÂNGULOS DE 60 em 60°.

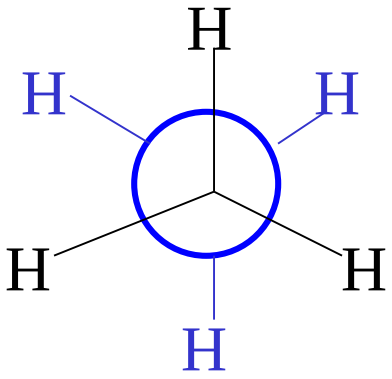


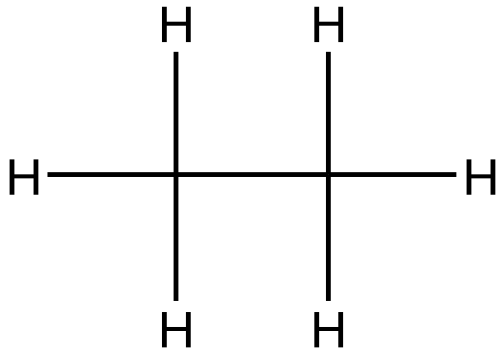


ANÁLISE CONFORMACIONAL: ETANO







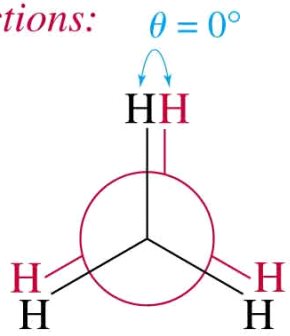


ANÁLISE CONFORMACIONAL: ETANO

-ECLIPSADAS: 0º entre os substituintes próximos: maior energia (menos estável).

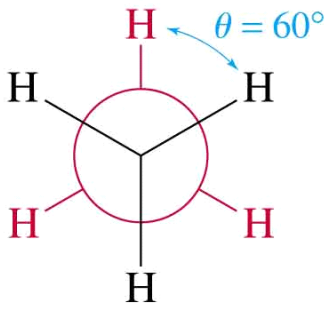
-ALTERNADAS: 60° entre os substituintes próximos: menor energia (mais estável).

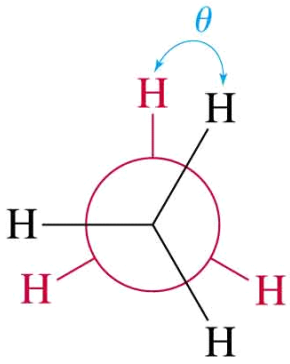
Newman projections:



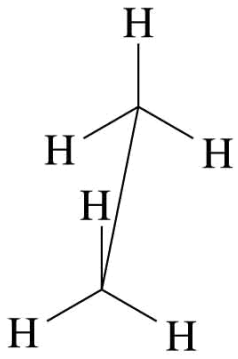
ECLIPSADAS

ALTERNADAS

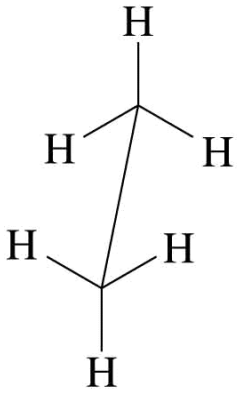




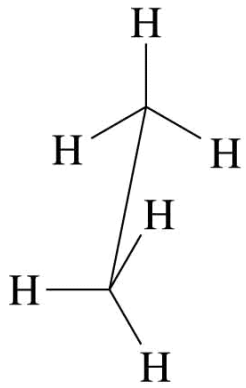
Sawhorse structures:



eclipsed, $\theta = 0°$



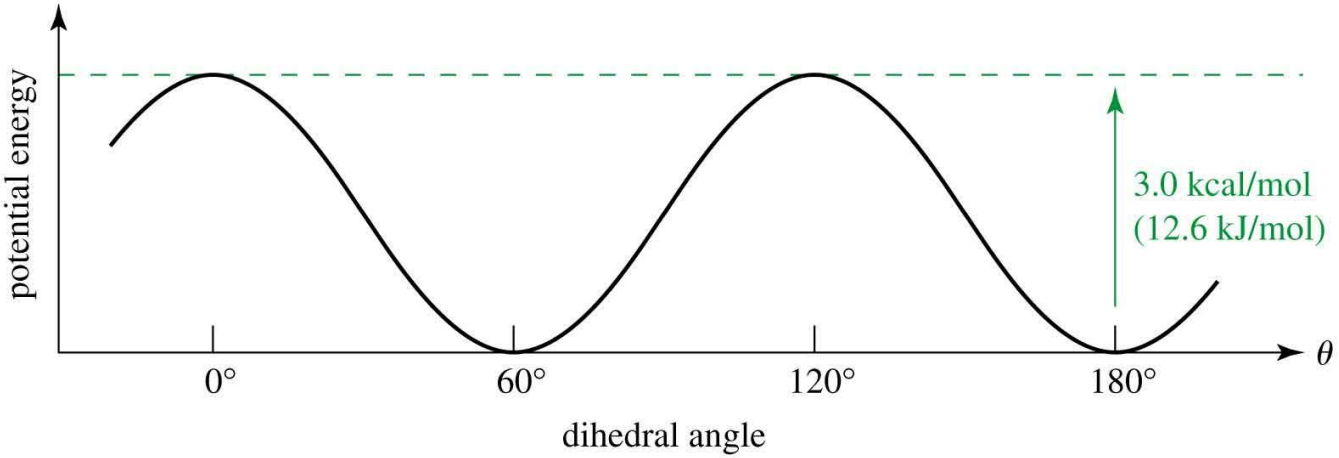
staggered, $\theta = 60°$

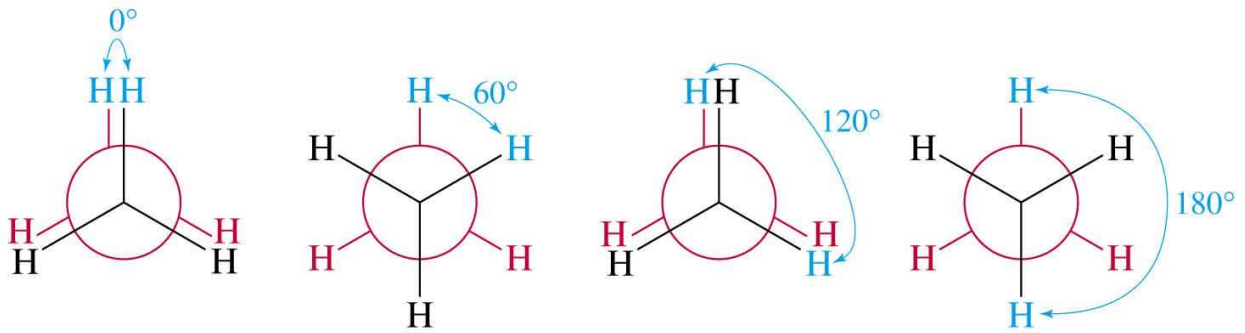


skew, θ = anything else

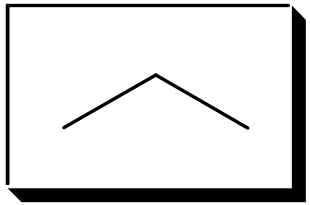
ANÁLISE CONFORMACIONAL ETANO: ENERGIA

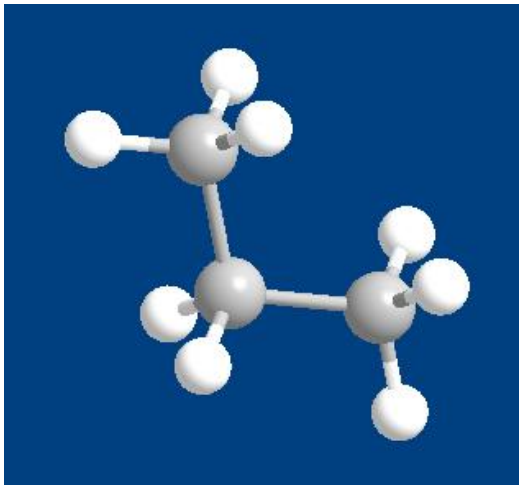
- Tensão torsional: resistência a rotação (proximidade de grupos).
- Para etano, apenas 3.0 kcal/mol

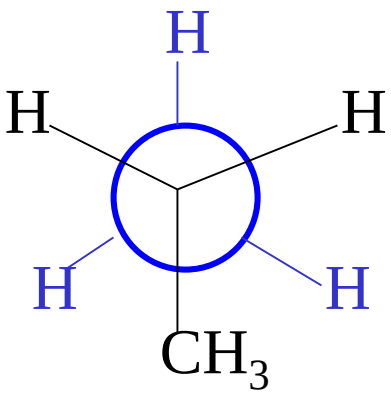


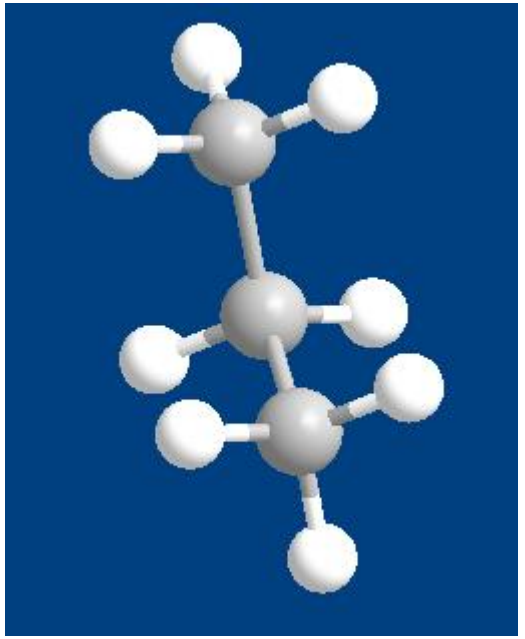


ANÁLISE CONFORMACIONAL: PROPANO

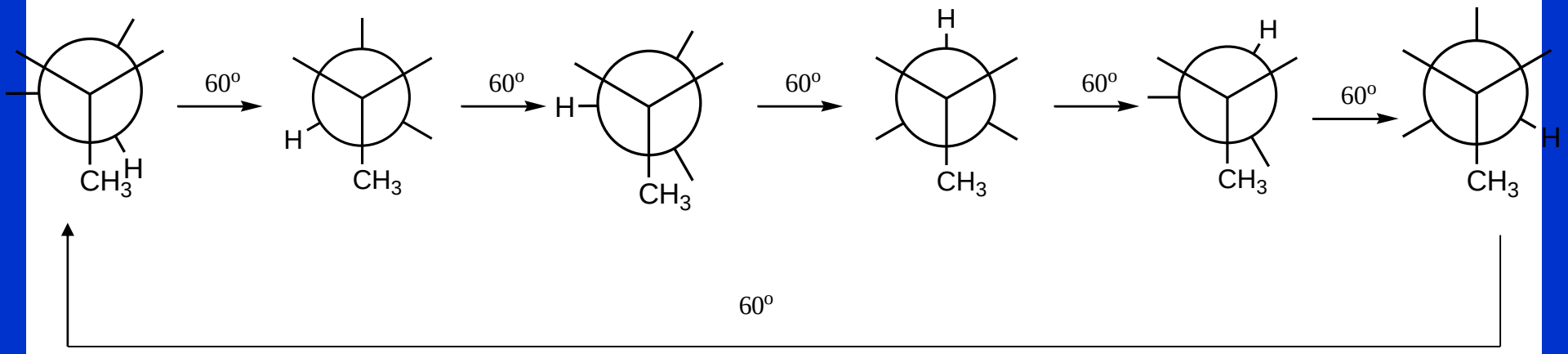








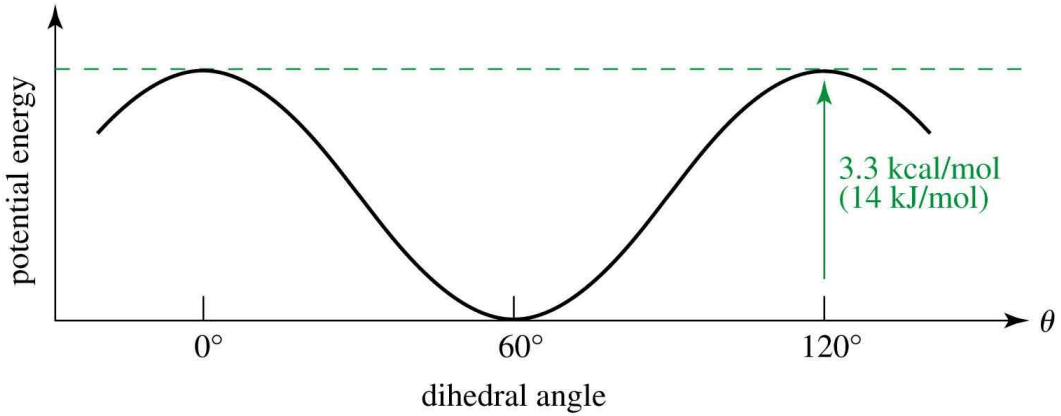
ANÁLISE CONFORMACIONAL: PROPANO

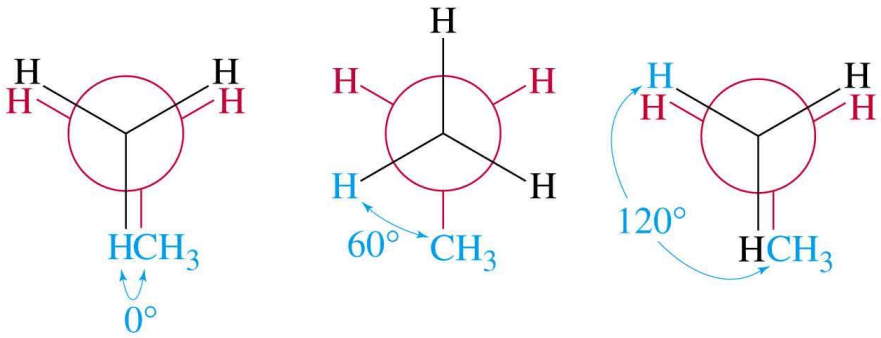


CONFÔRMEROS

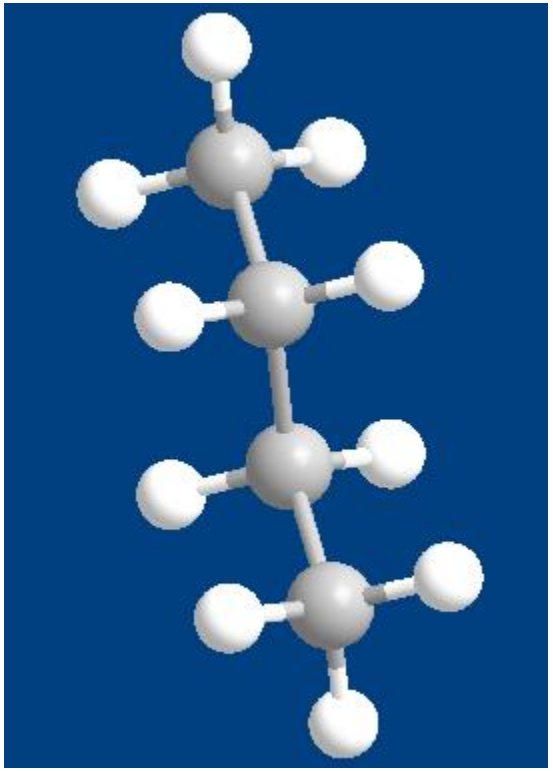
ANÁLISE CONFORMACIONAL PROPANO: ENERGIA

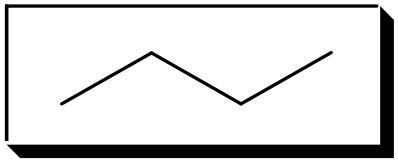
Aumento na tensão torsional devido ao grupo mais Impedido metila (comparado com etano).

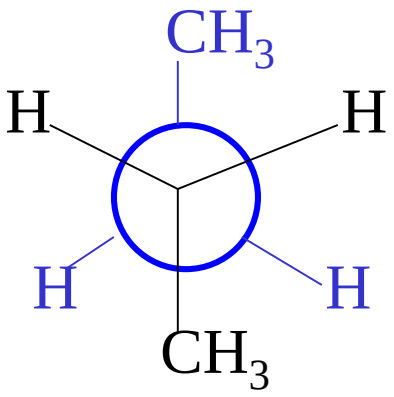


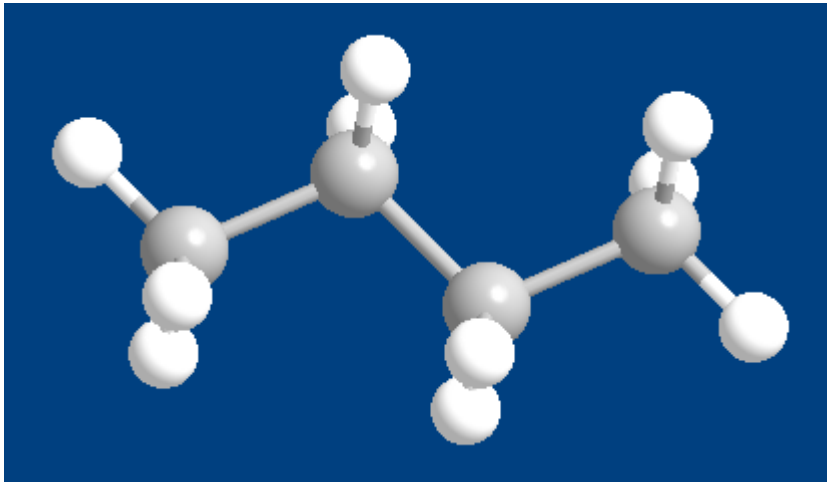


ANÁLISE CONFORMACIONAL: BUTANO



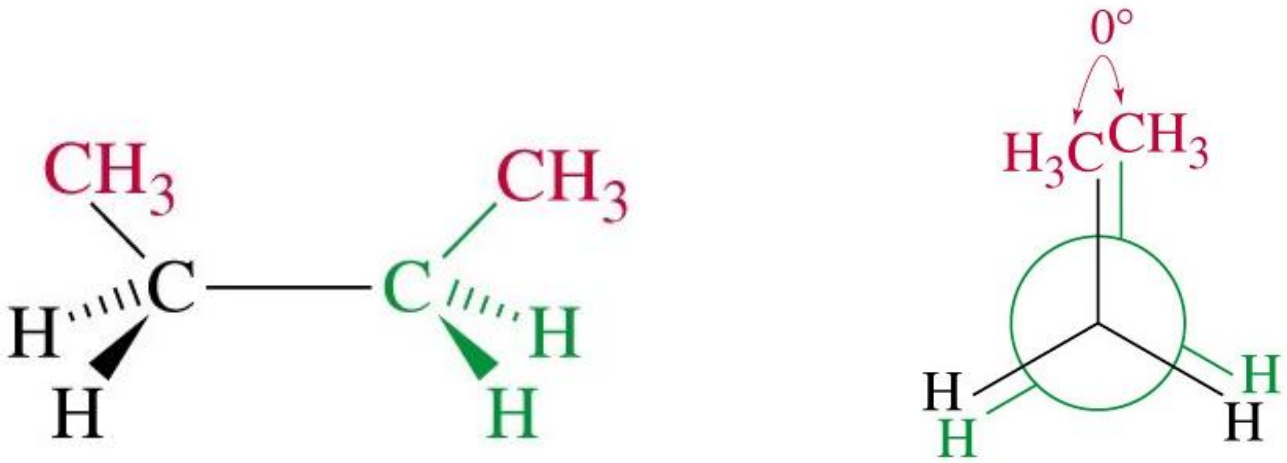






ANÁLISE CONFORMACIONAL BUTANO (1)

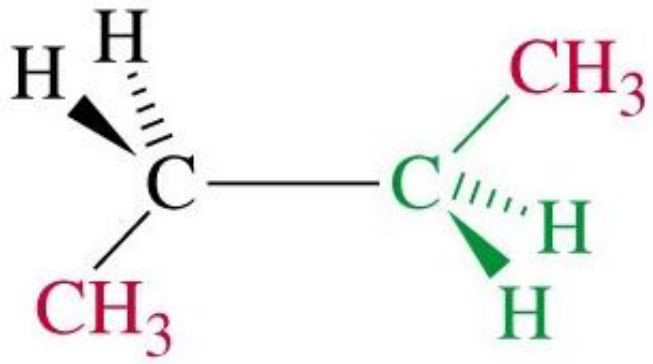
- Maior energia tem os grupos metilas eclipsados.
- Alta tensão estérica
- Ângulo entre as metilas = 0º



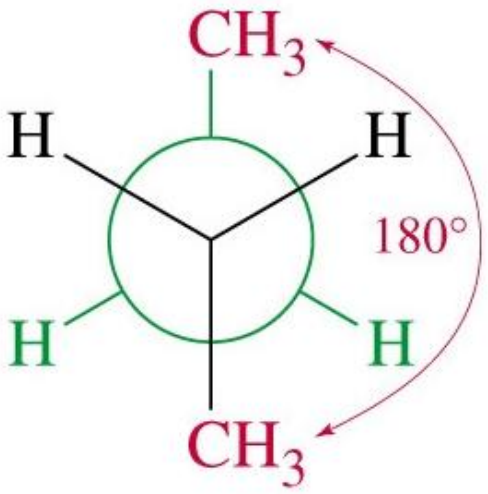
Totalmente eclipsada

ANÁLISE CONFORMACIONAL BUTANO (2)

- Menor energia entre as metilas anti (mais afastadas).
- Menor tensão estérica
- Ângulo entre as metilas = 180º

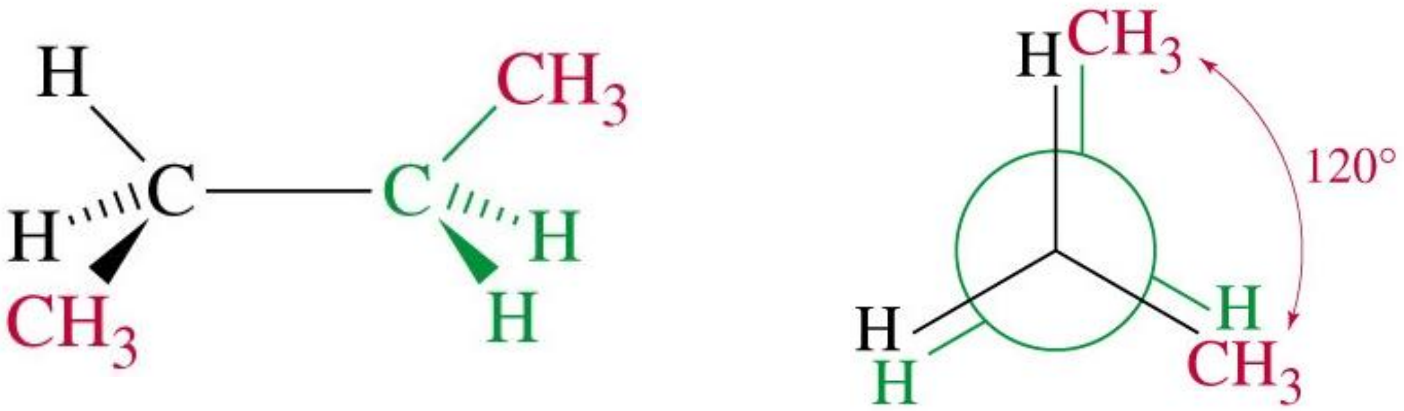


anti



ANÁLISE CONFORMACIONAL BUTANO (3)

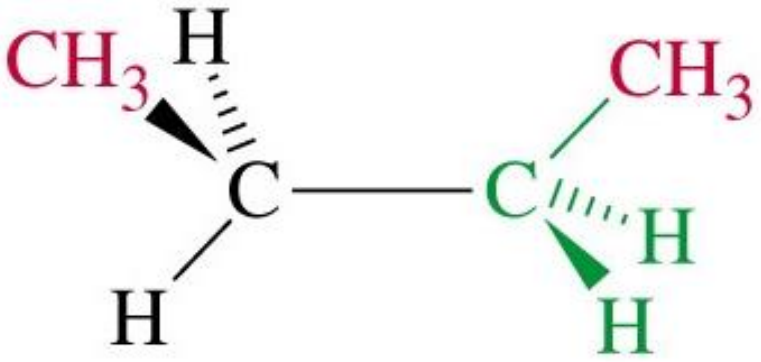
- Grupos metilas eclipsados com Hidrogênio
- Maior energia (tensão estérica) que a anti
- Ângulo entre as metilas = 120º

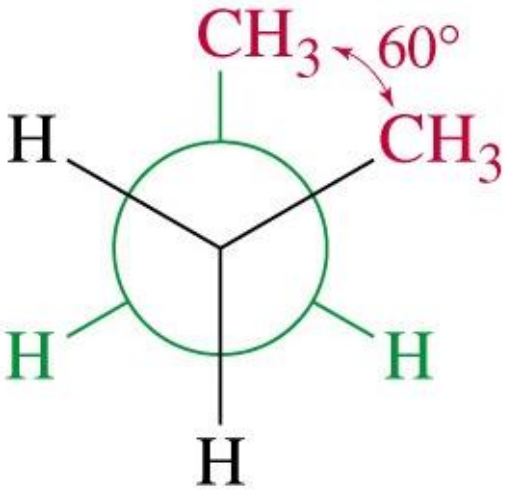


eclipsada

ANÁLISE CONFORMACIONAL BUTANO (4)

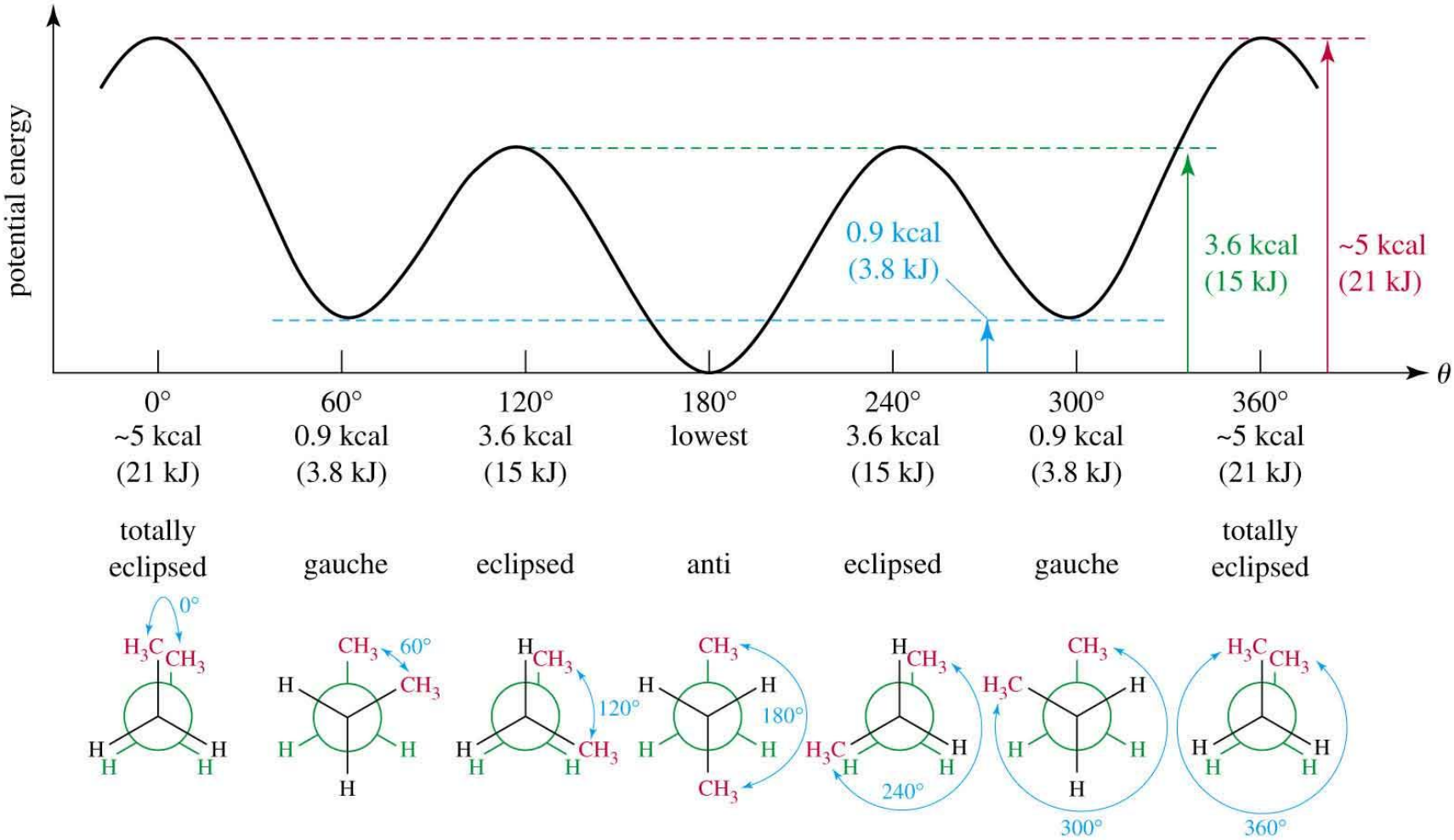
- Conformação Gauche é uma conformação alternada que não é a anti
- Metilas mais próximas que na conformação anti
- Ângulo entre as metilas = 60°





gauche

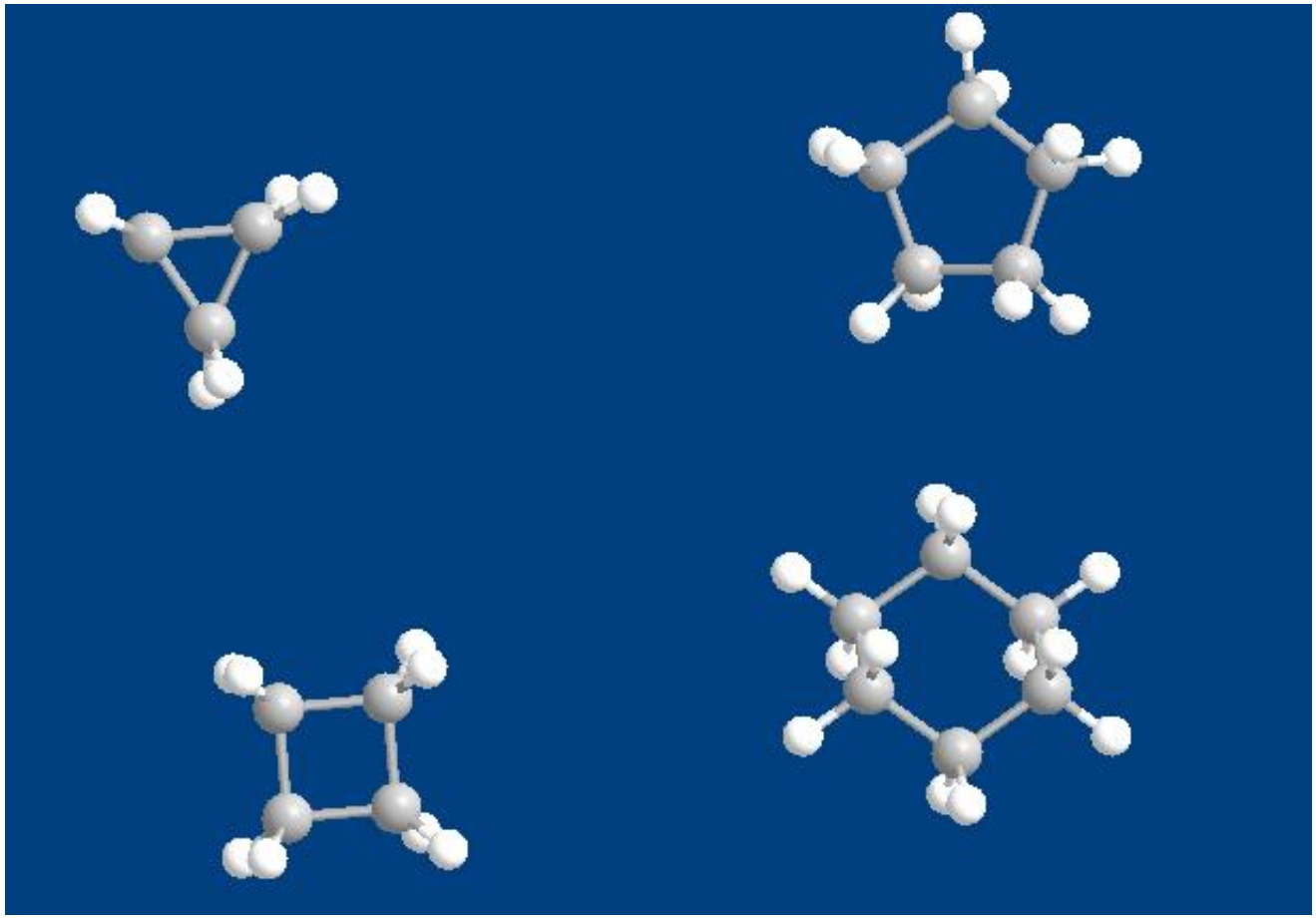
ANÁLISE CONFORMACIONAL PROPANO: ENERGIA



Exercício

- Desenhe projeção de Newman para a conformação mais e menos estável do butano.

ANÁLISE CONFORMACIONAL: CICLOALCANOS



ANÁLISE CONFORMACIONAL EM CICLOALCANOS: ESTABILIDADE

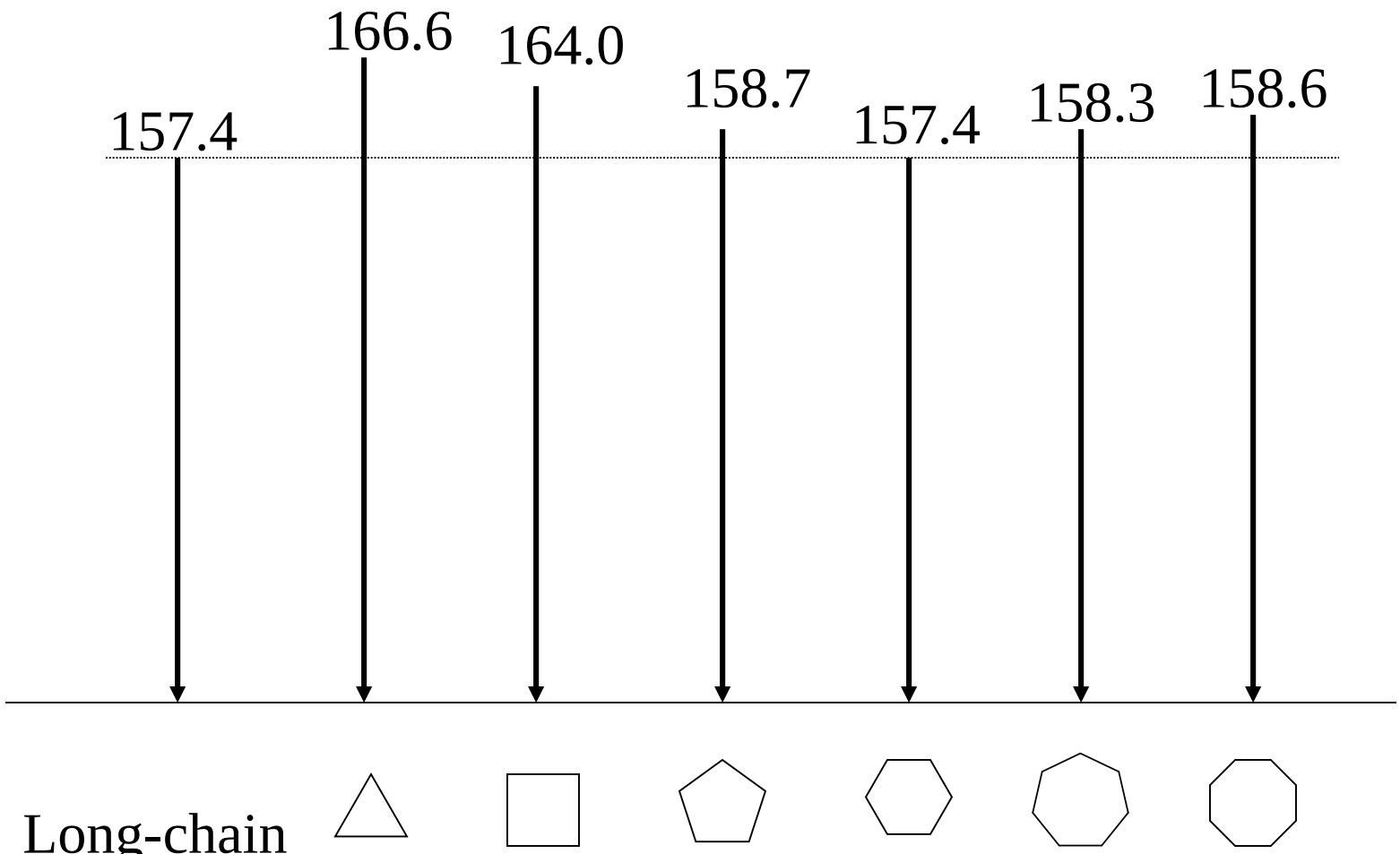
- Tensão angular: Em determinados anéis o ângulo de ligação tem tendência a apresentar valor menor do ângulo ideal para a hibridização sp^3 (109.5º). Esta diferença corresponde a tensão angular.

- Medida pela calor de combustão.

- Analisa-se as demais tensões de alcanos acíclicos.

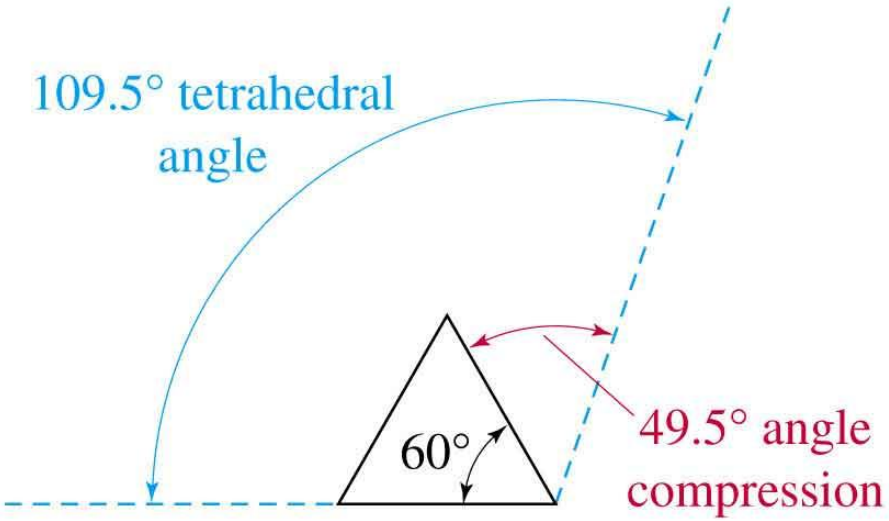
Calor de combustão

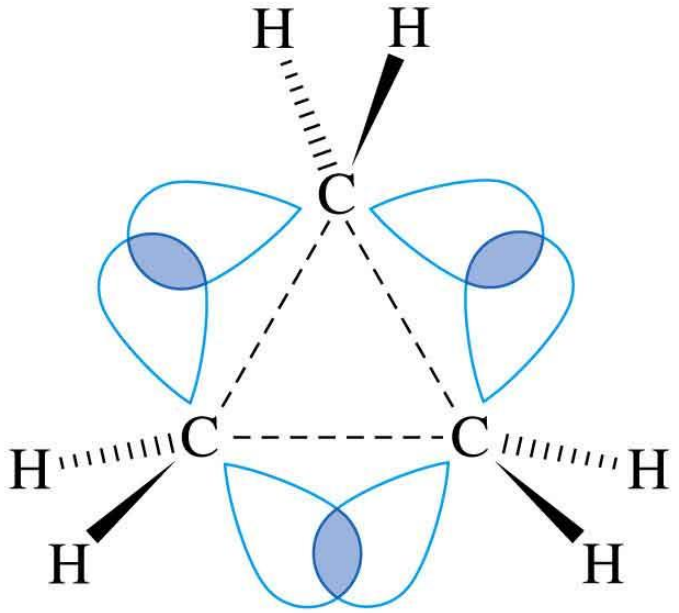
Alcano + $O_2 \rightarrow CO_2 + H_2O$



ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOPROPANO

- Alta tensão angular devido ao ângulo de ligação (60º)
- Muito reativo, ligação fraca
- A sobreposição de orbitais não é efetiva

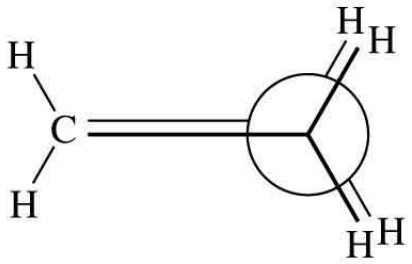




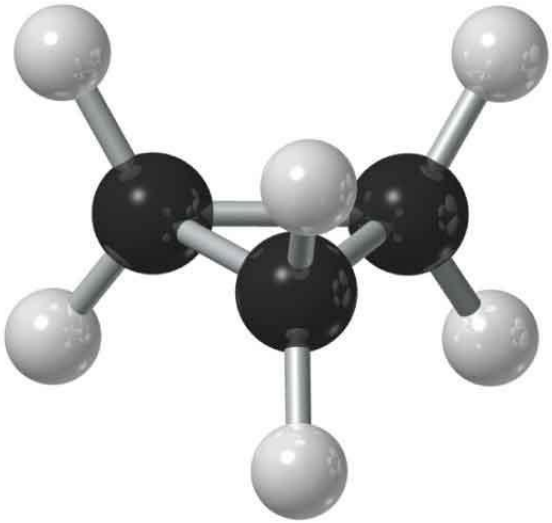
"bent bonds"
nonlinear overlap

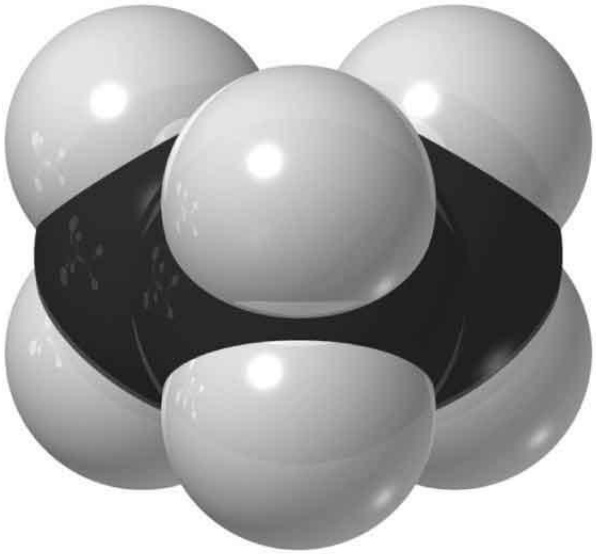
ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOPROPANO

Tensão torsional devido a proximidade dos hidrogênios



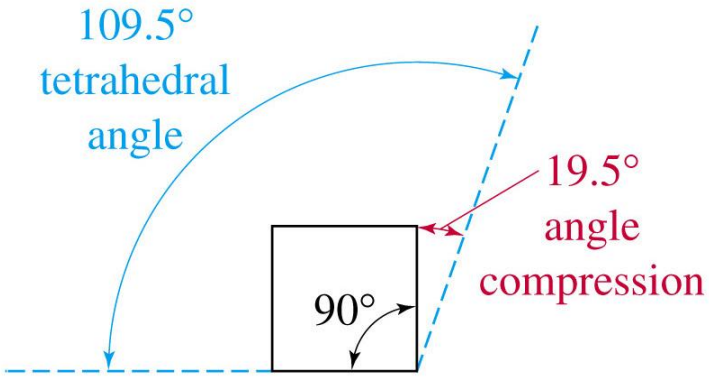
Newman projection of cyclopropane

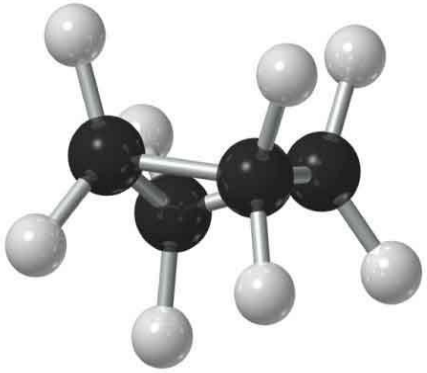


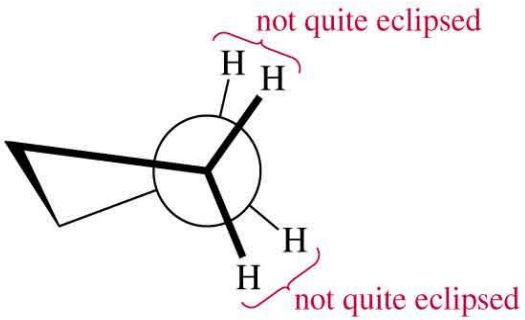


ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOBUTANO

- Tensão angular (90º)
- Tensão torsional aliviada devido a distorção do anel.



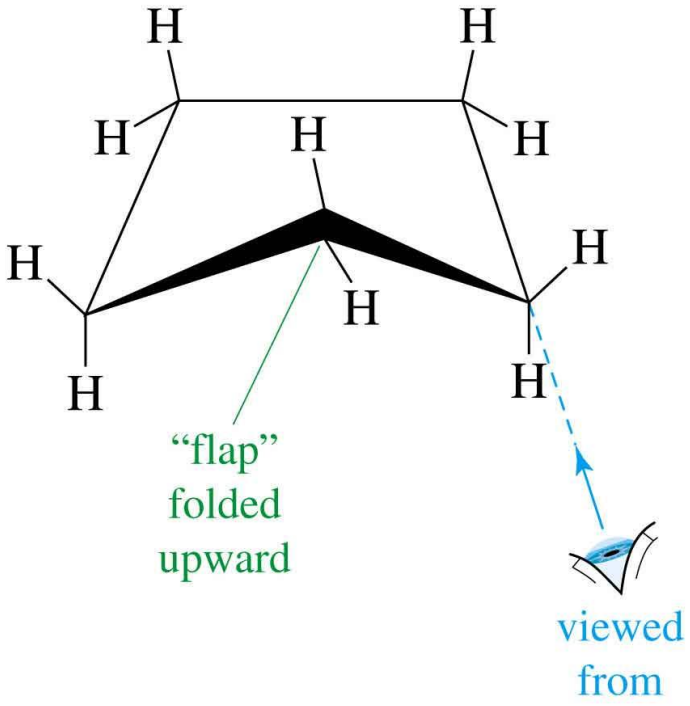


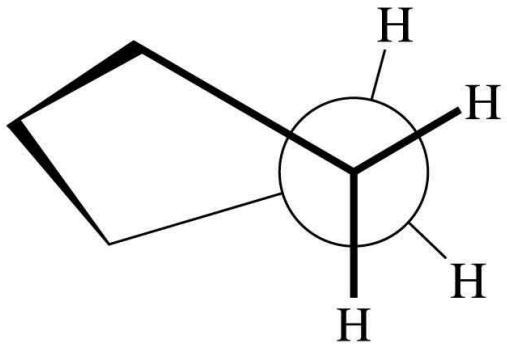


Newman projection of one bond

ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOPENTANO

- Estrutura distorcida (não-planar) – 108º
- Distorção diminui a tensão angular e a tensão torsional.





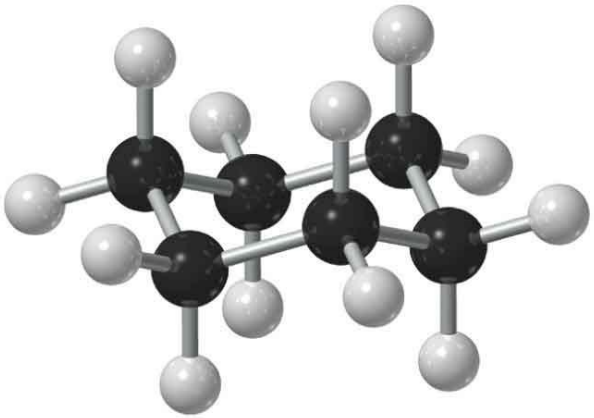
Newman projection showing relief of eclipsing of bonds

=>

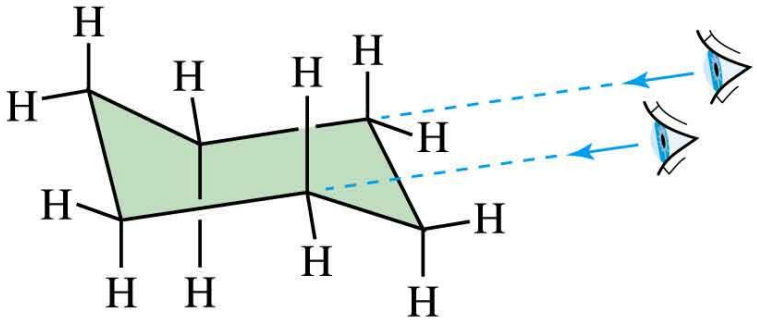
ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOEXANO

- Dados de combustão indica que o sistema não é tensionado
- Na conformação cadeira, todos os ângulos são de 109,5º e os H estão alternados.
- Não há tensão angular e nem tensão torsional.

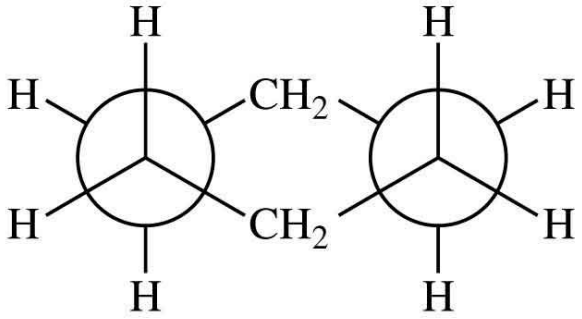
ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOEXANO – CONFORMAÇÃO CADEIRA



chair conformation



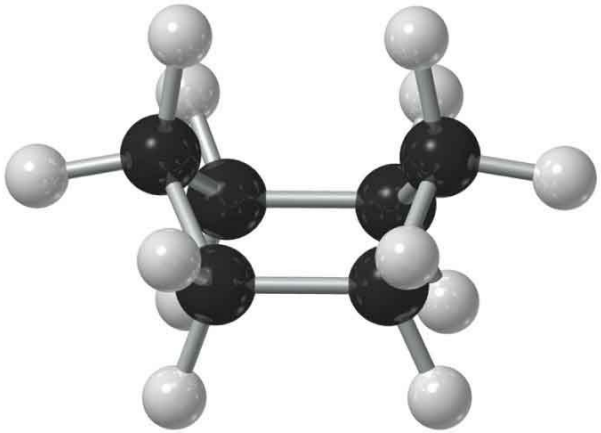
viewed along the “seat” bonds



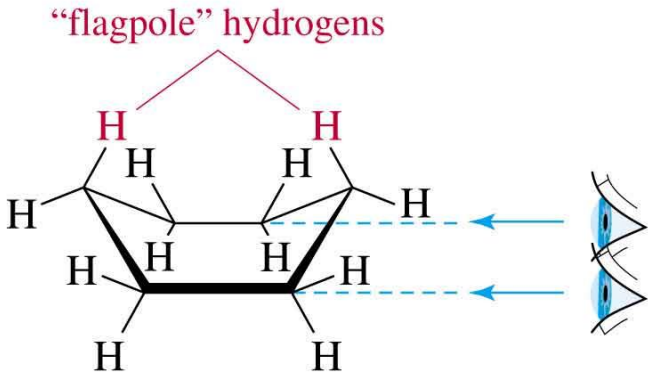
Newman projection

=>

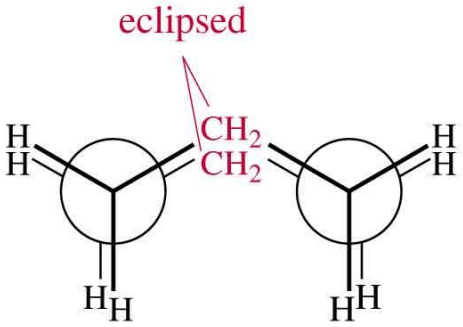
ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOEXANO – CONFORMAÇÃO BOTE (Barco)



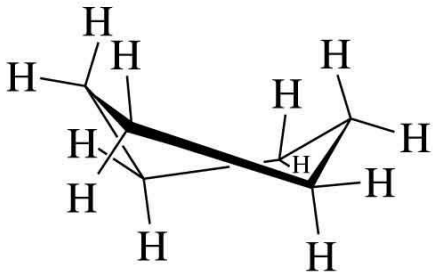
boat conformation



symmetrical boat



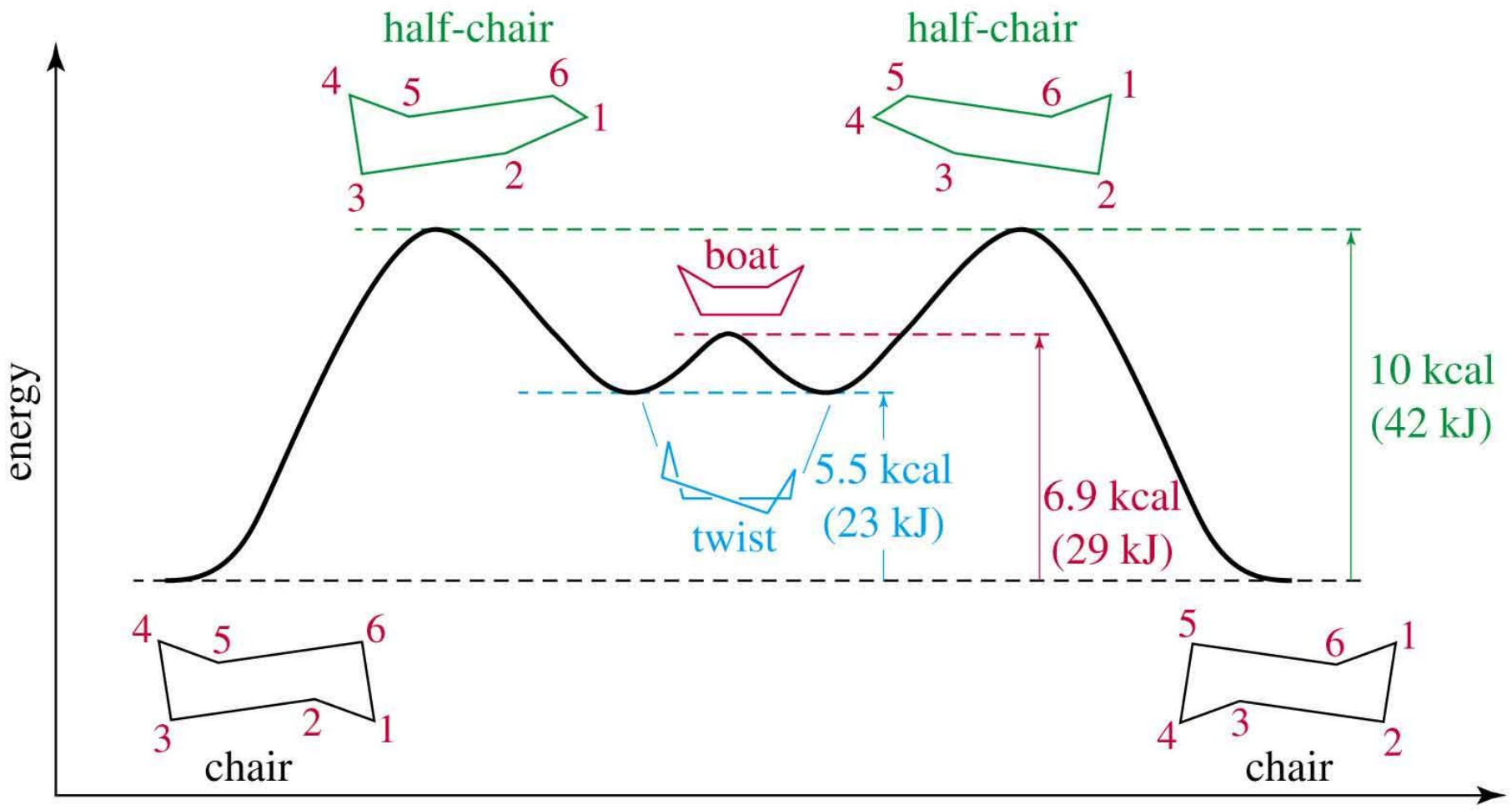
Newman projection



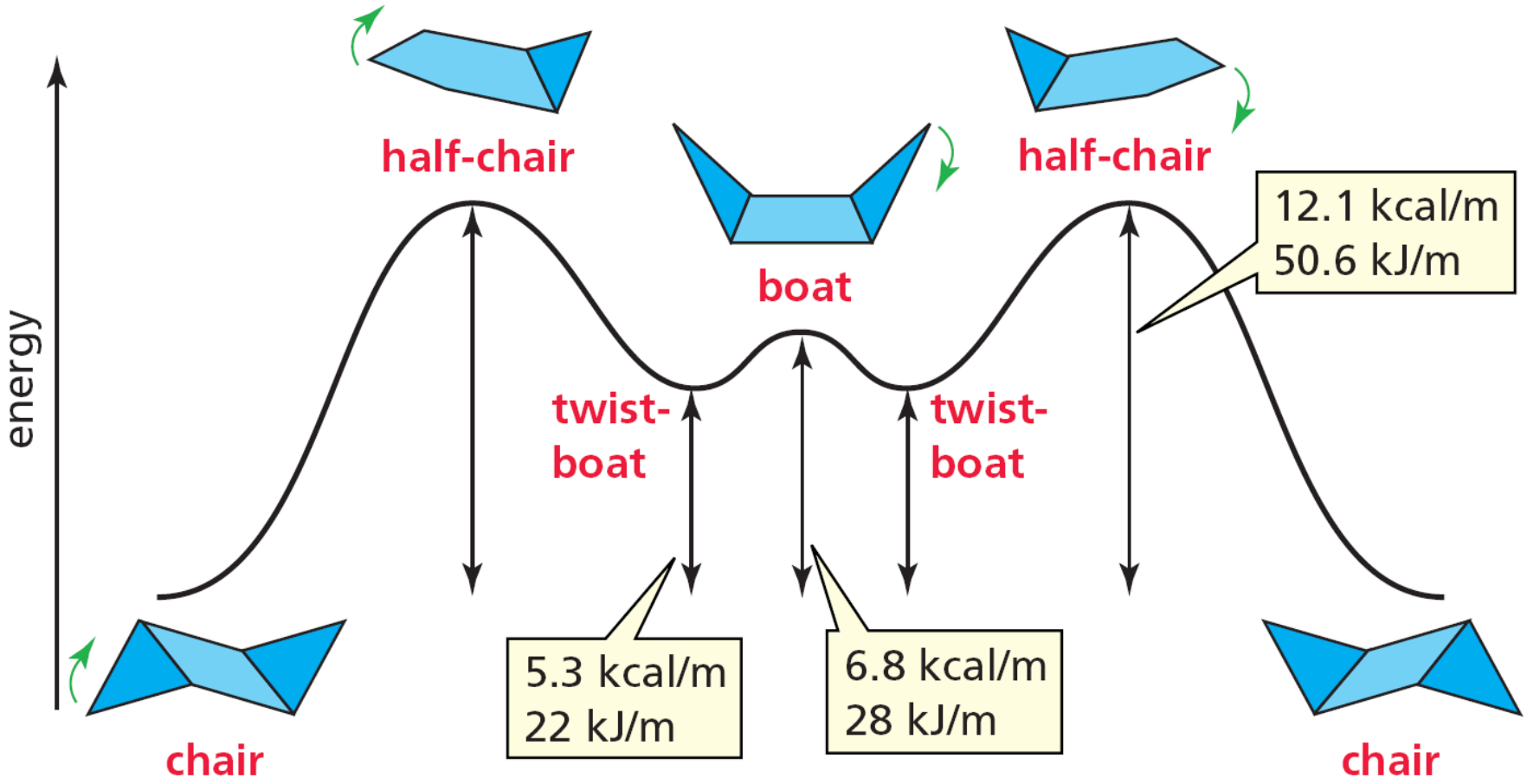
"twist" boat

=>

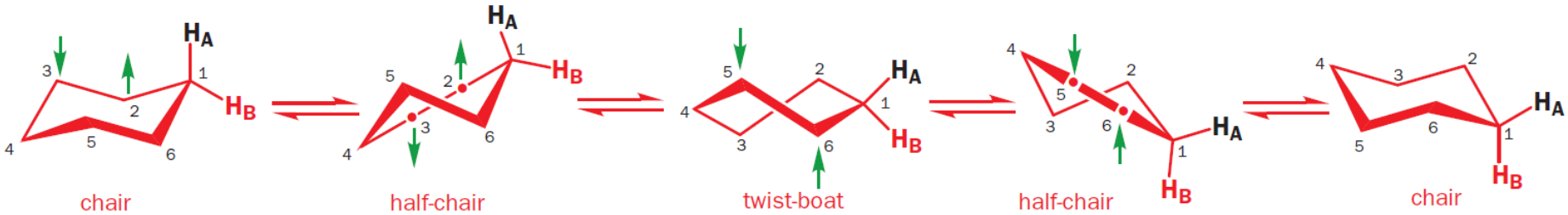
ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOEXANO – ENERGIAS

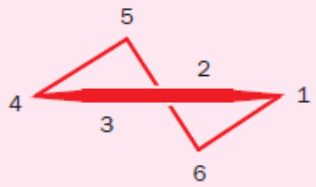


ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOEXANO – ENERGIAS



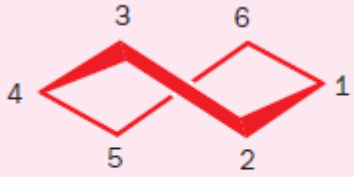
Desenhando as conformações para o cicloexano





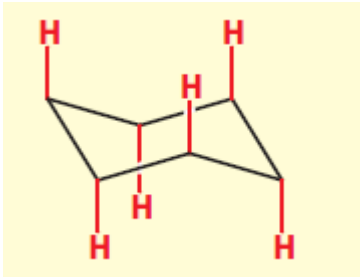
the easiest way of drawing a half-chair. Carbons 1–4 are all in the same plane

an alternative perspective of a half-chair conformation



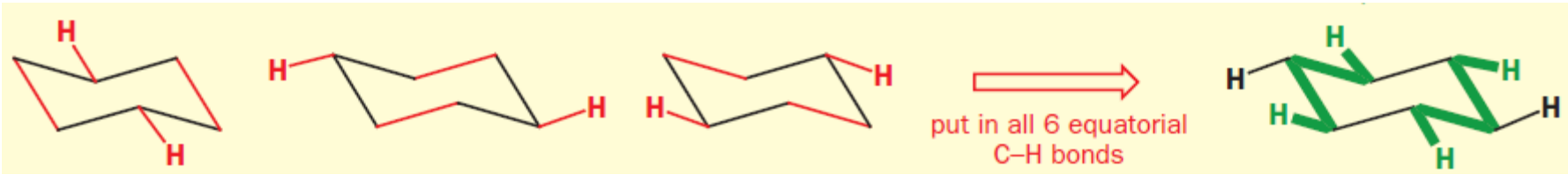
the easiest way to draw a twist-boat conformation. . .

. . . although it's easier to see why it's called a twist boat from this viewpoint



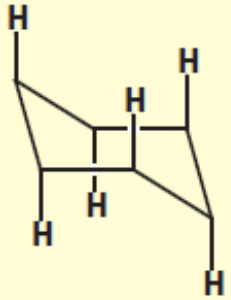
Colocando os Hs axiais

Colocando Hs equatoriais

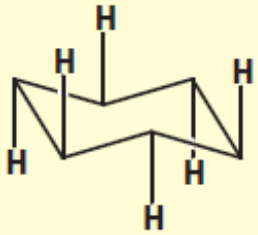


M e W

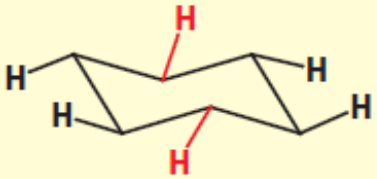
Erros comuns



the chair has been drawn with the middle bonds horizantal, so the upper points of the chair are not level. This means the axial hydrogens can no longer be drawn vertical

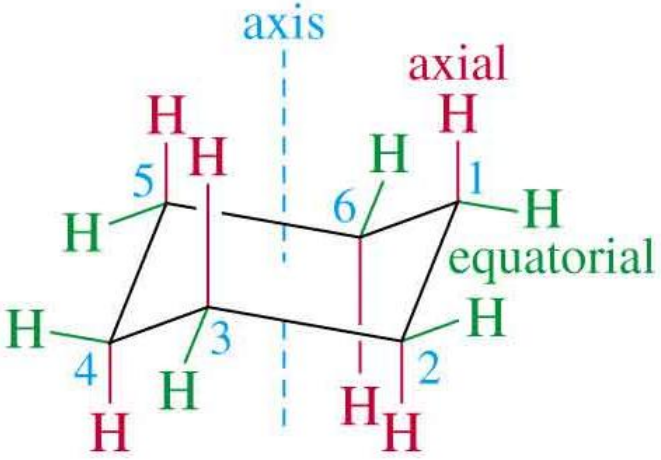


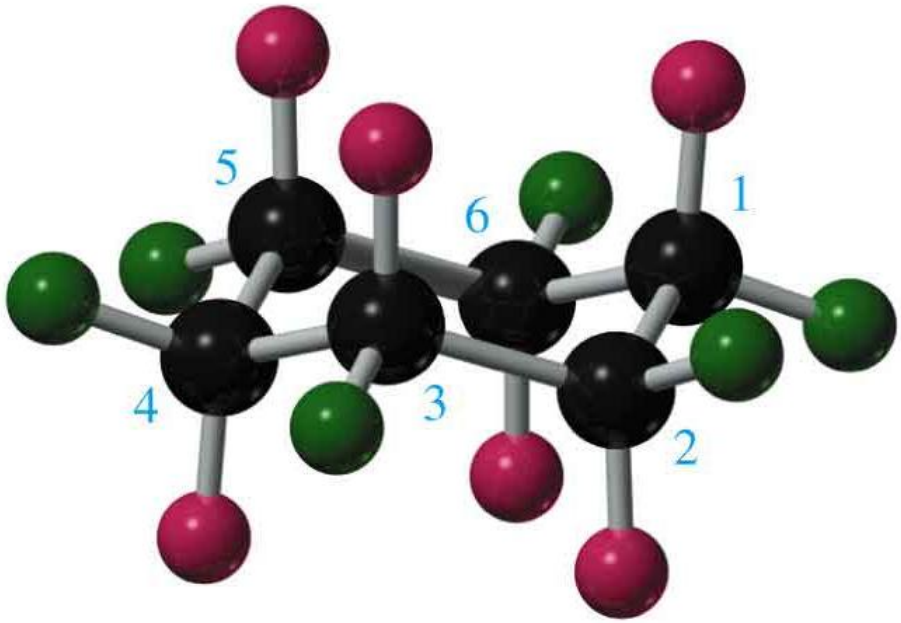
the axial hydrogens have been drawn alternating up and down on the wrong carbons. This structure is impossible because none of the carbons can be tetrahedral



the red hydrogens have been drawn at the wrong angles – look for the parallel lines and the 'W' and 'M'

ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOEXANO – H Axiais e Equatoriais





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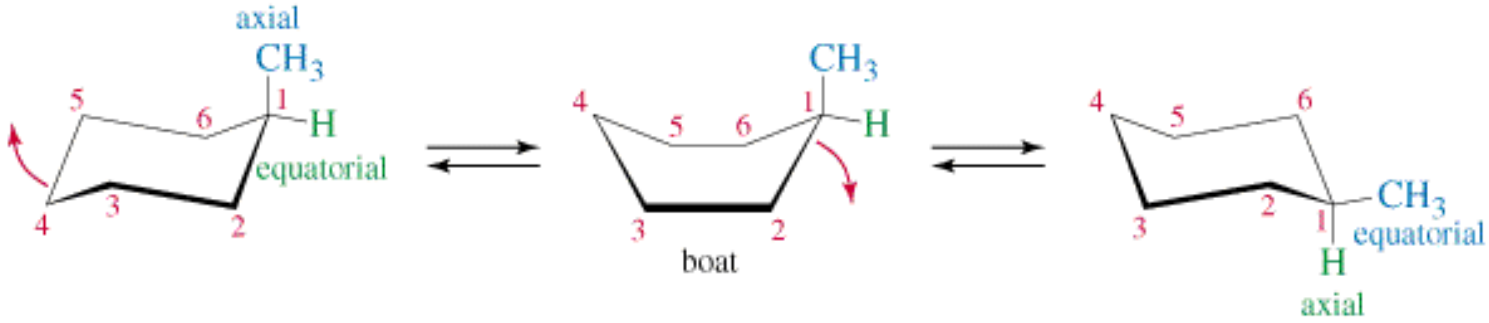
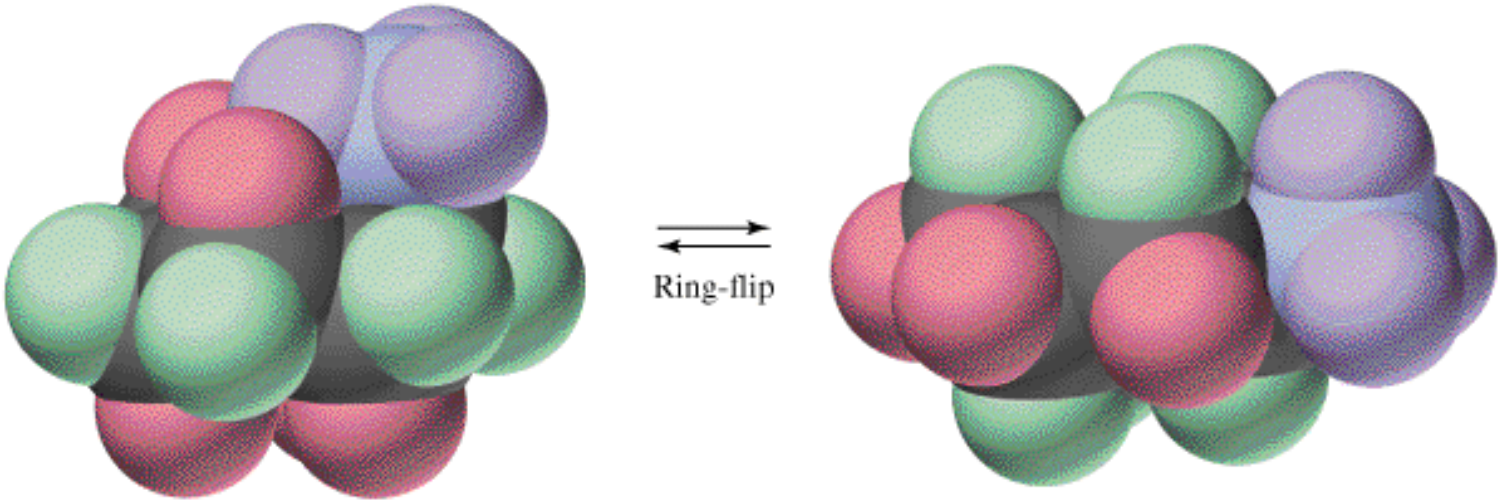
ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOEXANO – MONOSUBSTITUÍDO





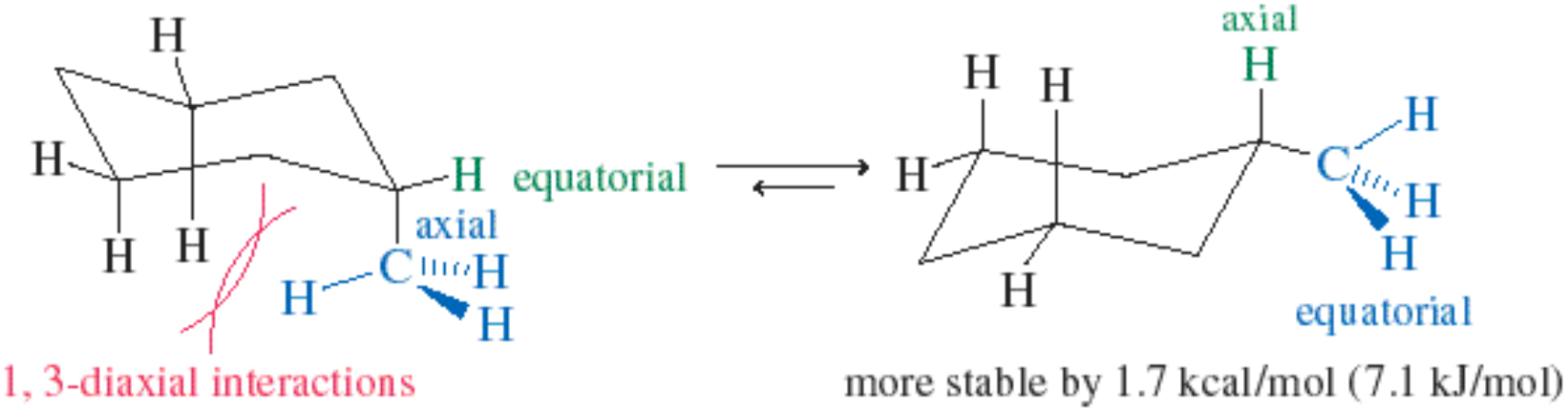
CH_3 axial

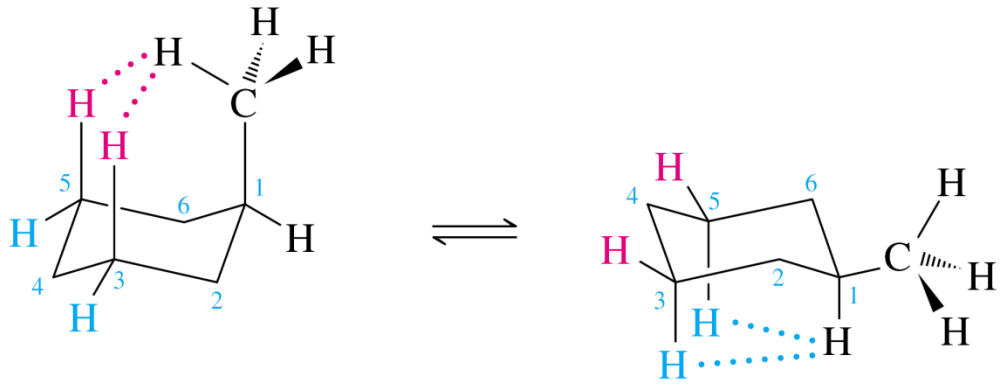
CH_3 equatorial

=>

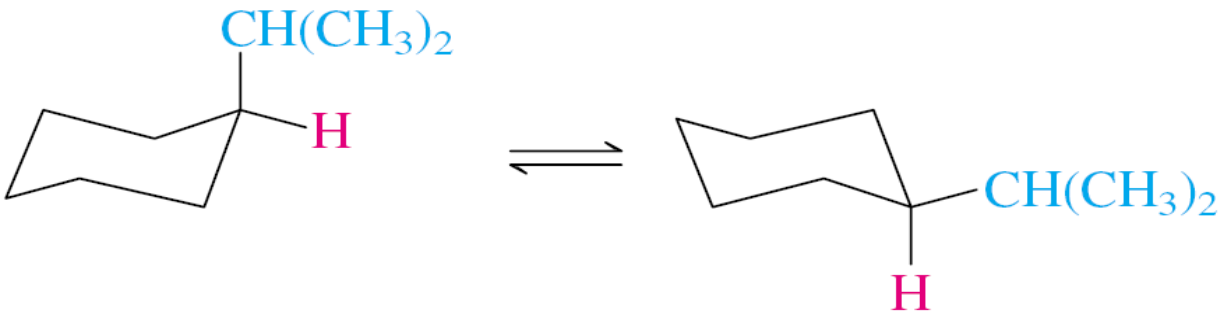
ANÁLISE CONFORMACIONAL EM CICLOALCANOS: CICLOEXANO – MONOSUBSTITUÍDO

Posição equatorial com menor tensão estérica: mais estável para substituintes volumosos.

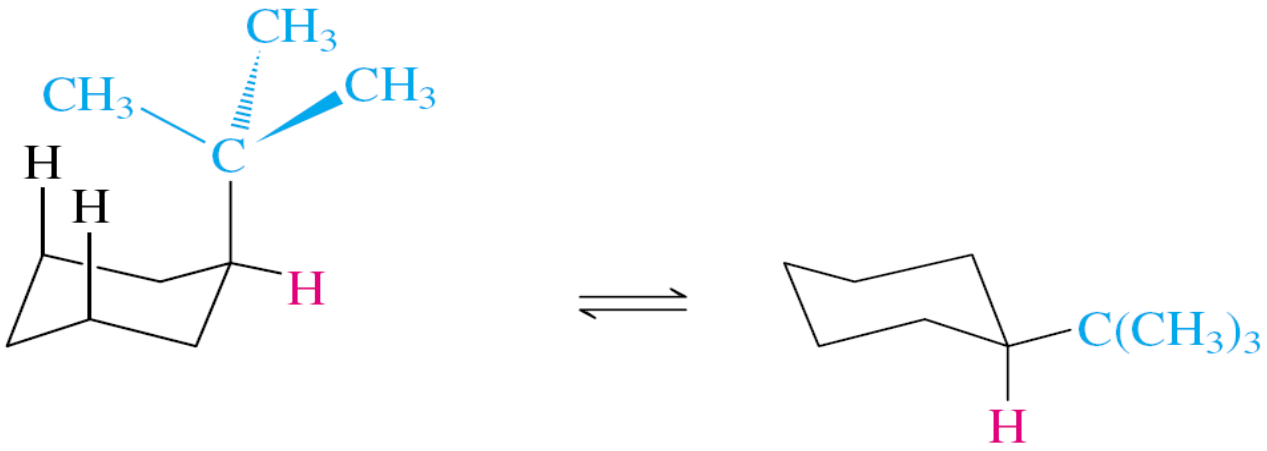




Interação estérica 1,3 diaxial é grande



3% 97%

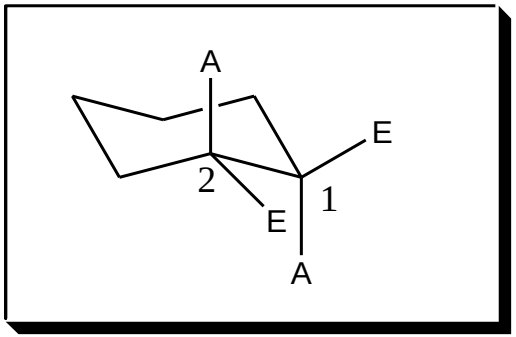


Less than 0.01%
(Serious 1,3-diaxial repulsions involving *tert*-butyl group)

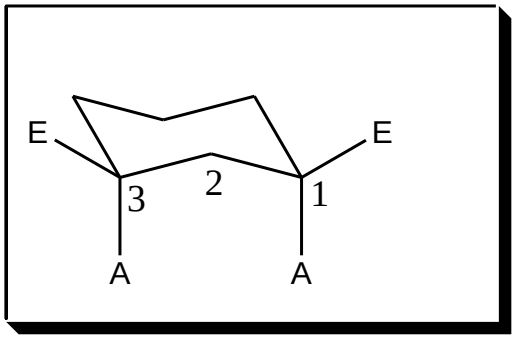
Greater than 99.99%
(Decreased van der Waals strain)

Quanto maior o volume estérico do substituinte, maior será a preferência pela posição equatorial

ANÁLISE CONFORMACIONAL EM CICLOEXANO DISUBSTITUÍDO

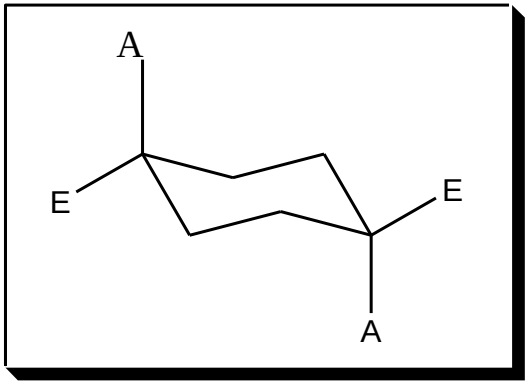


1,2



1,3

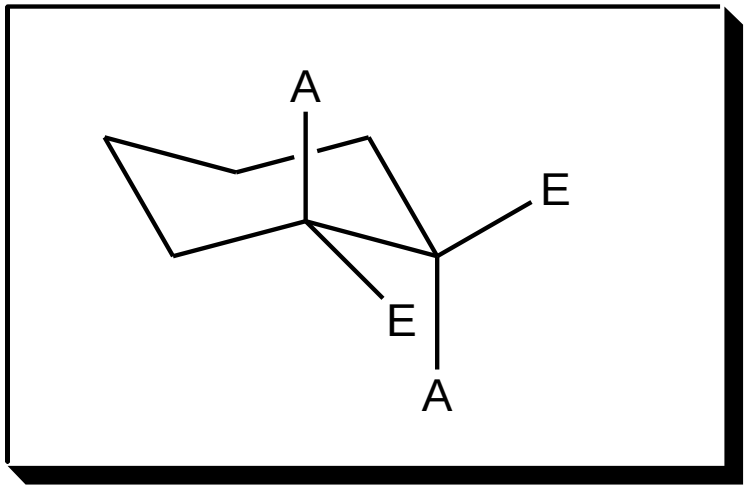
Exercício 1:
Qual a reação *cis/trans* entre os hidrogênios **equatoriais** nos cicloexanos 1,2; 1,3 e 1,4? Fazer o mesmo para o **axiais**!



1,4

Exercício 2:
Qual a reação *cis/trans* entre os hidrogênios **equatoriais-axiais** nos cicloexanos 1,2; 1,3 e 1,4? Fazer o mesmo para o axiais!

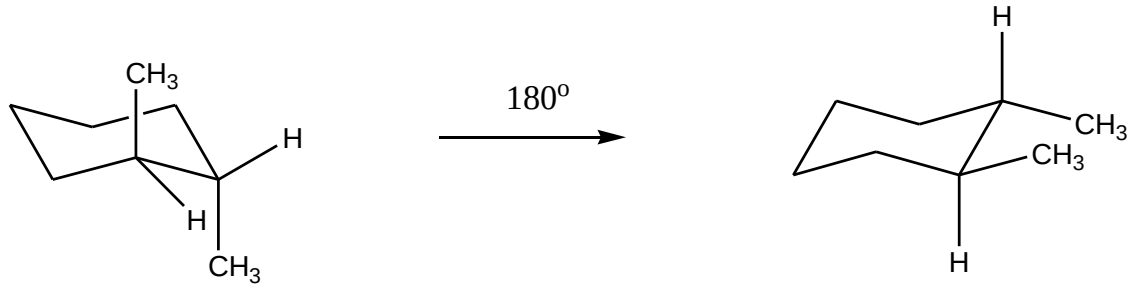
ANÁLISE CONFORMACIONAL EM CICLOEXANO 1,2-DISUBSTITUÍDO



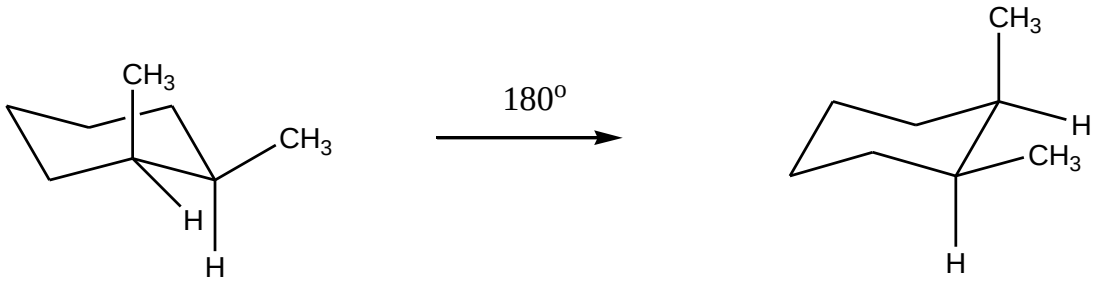
SUBSTITUINTES VOLUMOSOS OCUPANDO POSIÇÃO EQUATORIAL (MENOR TENSÃO ESTÉRICA) MAIS ESTÁVEL.

ANÁLISE CONFORMACIONAL EM CICLOEXANO 1,2-DISUBSTITUÍDO (IGUAIS)

1,2 - TRANS

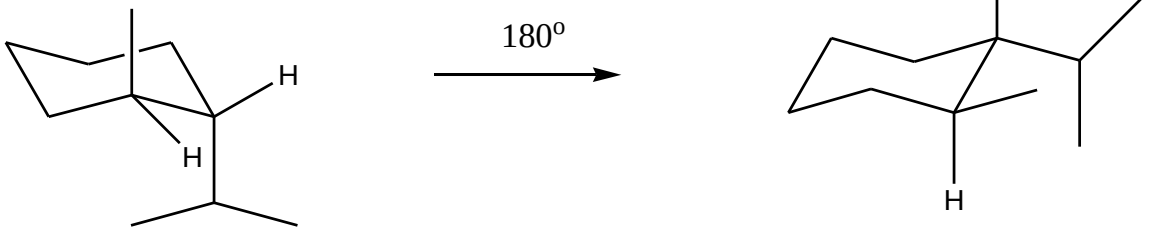


1,2 - CIS

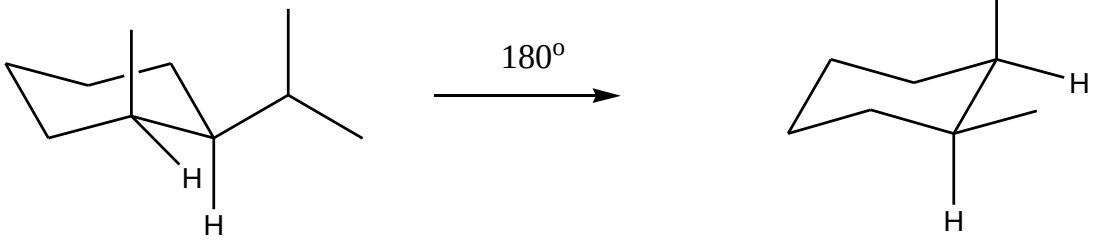


ANÁLISE CONFORMACIONAL EM CICLOEXANO 1,2-DISUBSTITUÍDO (DIFERENTES)

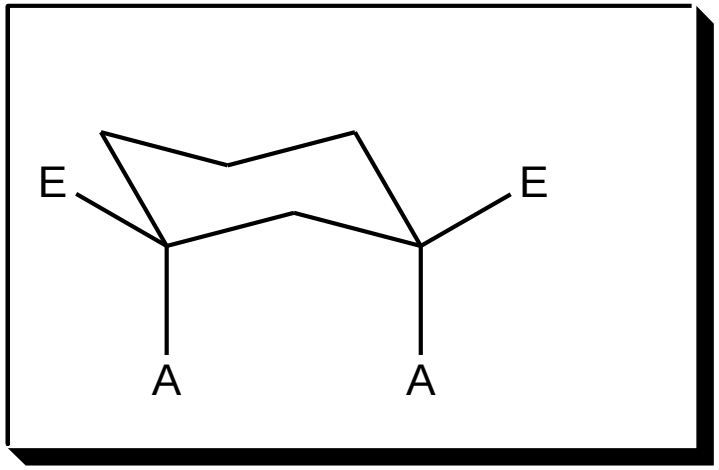
1,2 - TRANS



1,2 - CIS

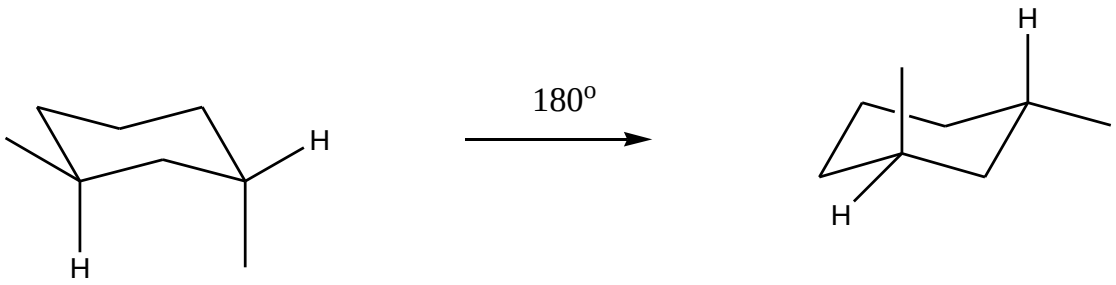


ANÁLISE CONFORMACIONAL EM CICLOEXANO 1,3-DISUBSTITUÍDO

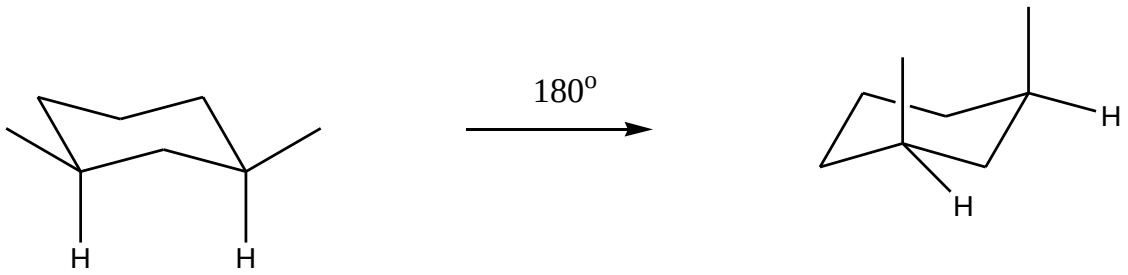


ANÁLISE CONFORMACIONAL EM CICLOEXANO 1,3-DISUBSTITUÍDO (IGUAIS)

1,3 - TRANS

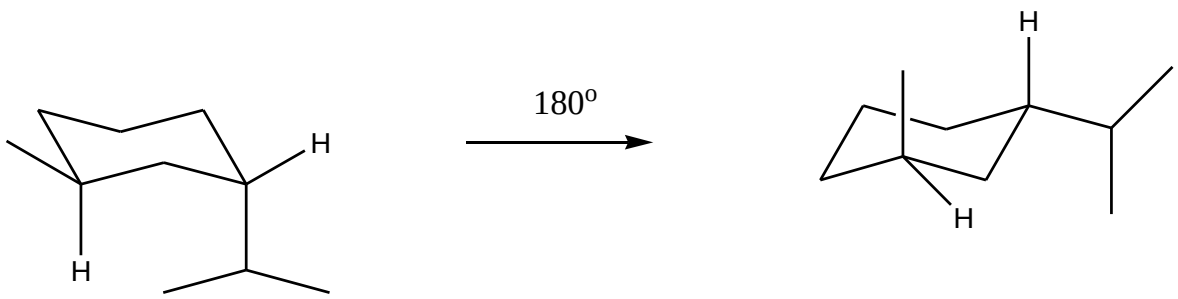


1,3 - CIS

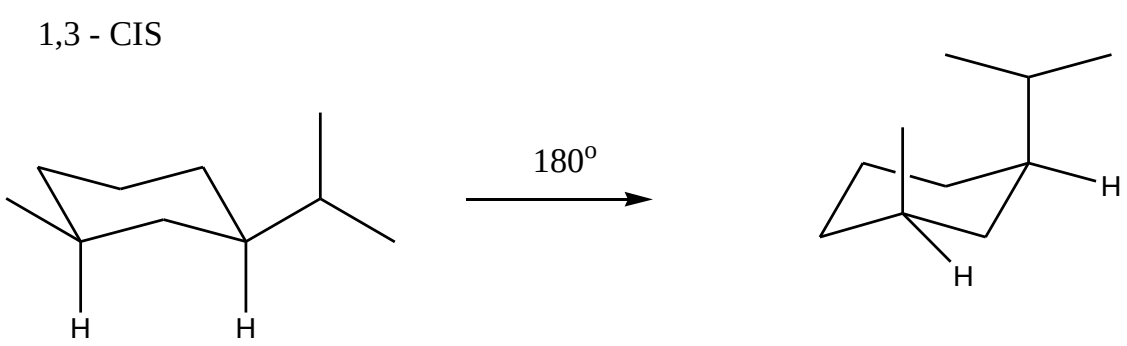


ANÁLISE CONFORMACIONAL EM CICLOEXANO 1,3-DISUBSTITUÍDO (DIFERENTES)

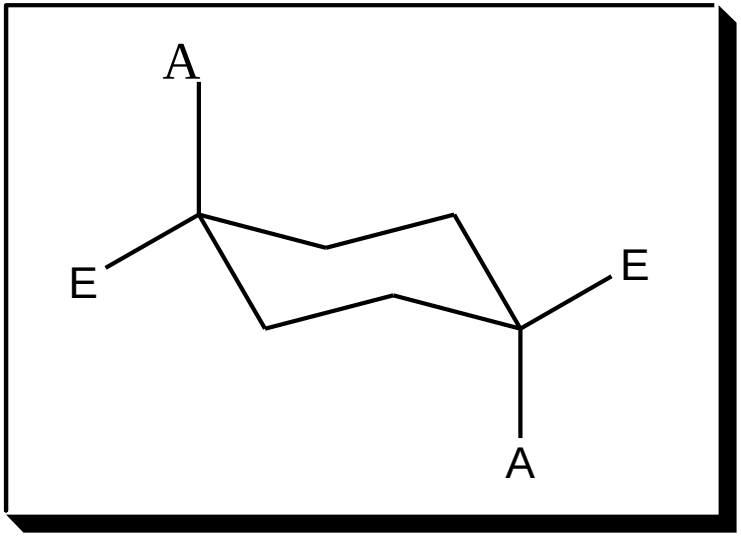
1,3 - TRANS



1,3 - CIS



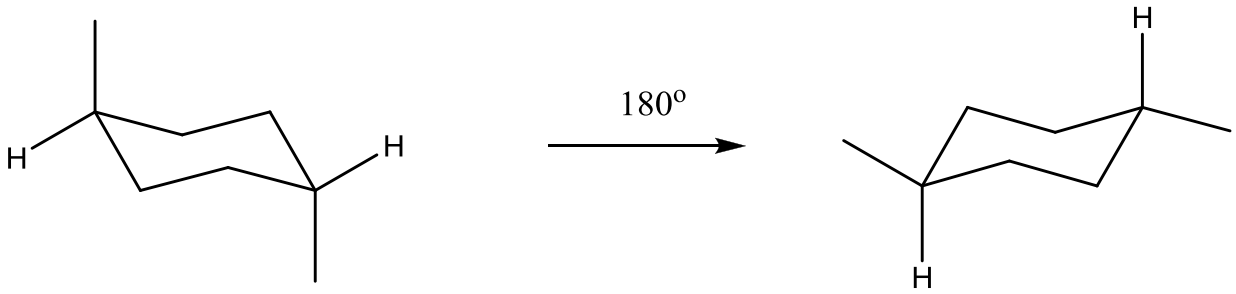
ANÁLISE CONFORMACIONAL EM CICLOEXANO 1,4-DISUBSTITUÍDO



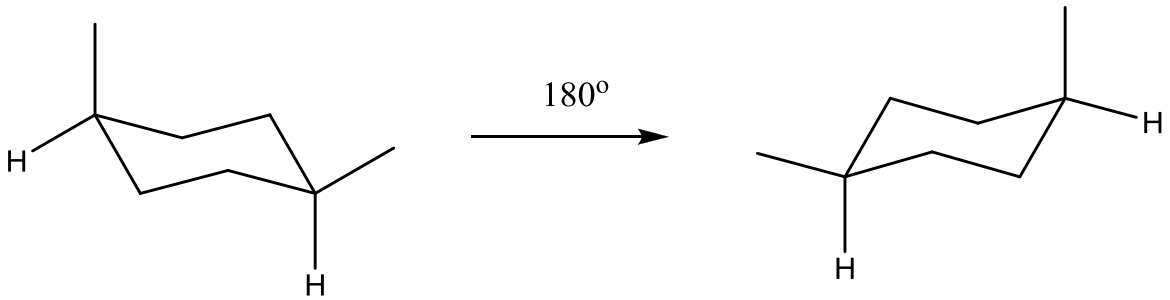
1,4

ANÁLISE CONFORMACIONAL EM CICLOHEXANO 1,4-DISUBSTITUÍDO (IGUAIS)

1,4 - TRANS

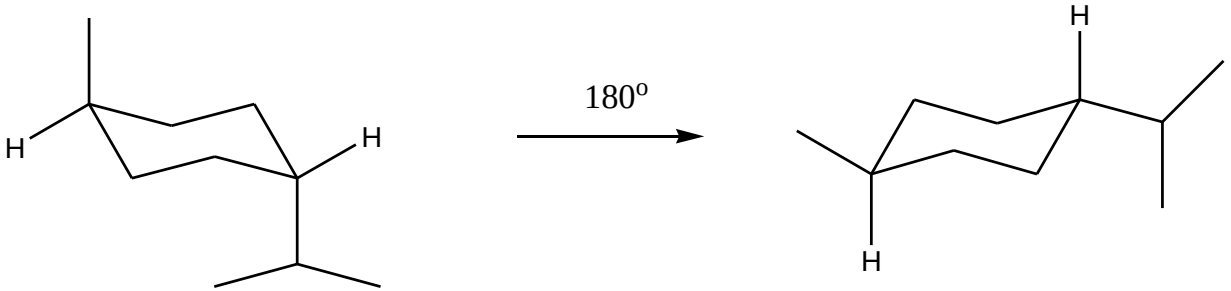


1,4 - CIS

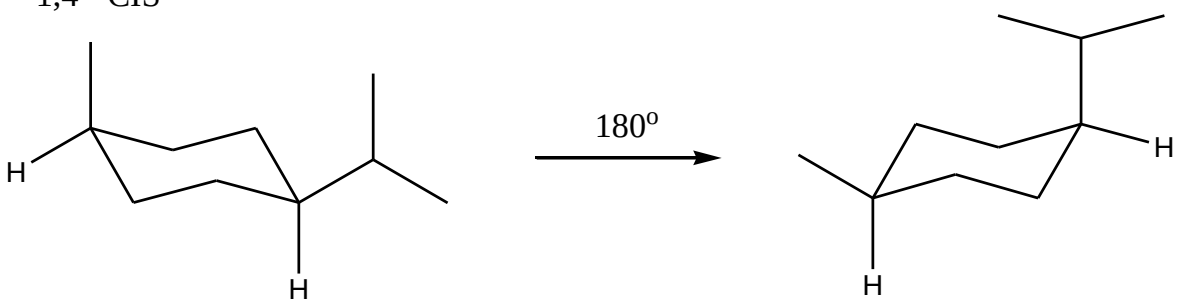


ANÁLISE CONFORMACIONAL EM CICLOHEXANO 1,4-DISUBSTITUÍDO (DIFERENTES)

1,4 - TRANS



1,4 - CIS



Exercício:

Escrever a estrutura da conformação mais estável e menos estável do estereoisômero do 1-*tert*-butil-3-metilcicloexano!

Exercício:

Desenhe a conformação mais estável da seguinte substância: