CHAPTER

24

Conformers

CONFORMATIONS OF ALKANES : ROTATION ABOUT CARBON-CARBON BONDS

In a **sawhorse projection,** you are looking at the carbon-carbon bond from an oblique angle. In a **Newman projection,** you are looking down the length of a particular carbon-carbon bond. The carbon in front is represented by the point at which three bonds intersect, and the carbon in back is reprsented by a circle.

The electrons in a carbon-hydrogen bond will repel the electrons in another carbon-hydrogen bond if the bonds get too close to each other. The **staggered conformation,** therefore, is the most stable conformation because the carbon-hydrogen bonds are as far away from each other as possible. The **eclipsed conformation** is the least stable conformation because in no other conformation are the carbon hydrogen bonds as close to one another. The extra energy of the eclipsed conformtion is called torsional strain. **Torsional strain** is the name given to the repulsion felt by the bonding electrons of one substituent as they pass close to the bonding electrons of an other substituent.

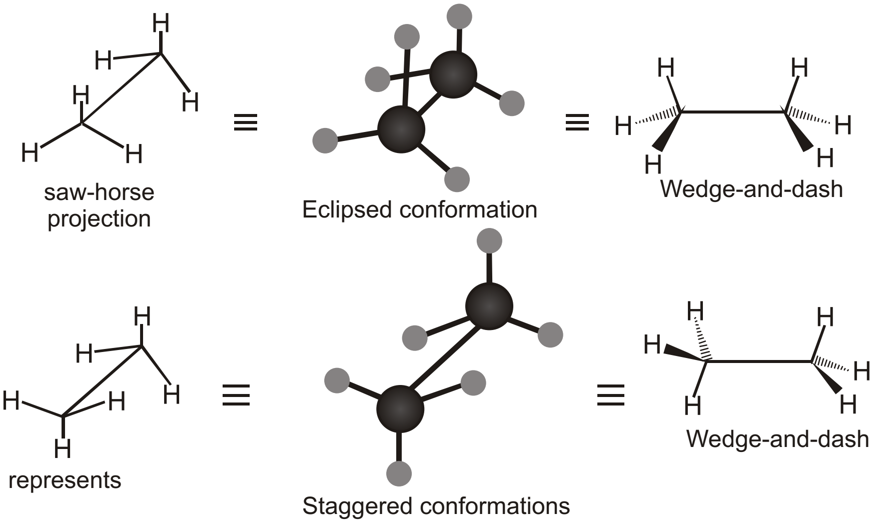


Fig. : Ethane in the eclipsed and staggered conformations.

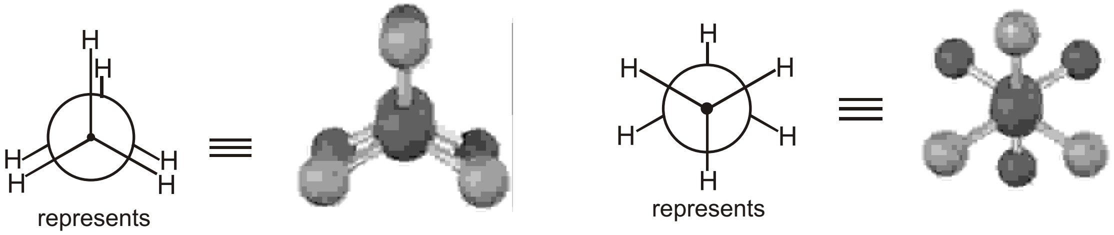
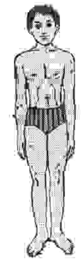


Figure : Newman projections of ethane in the eclipsed and staggered conformations.

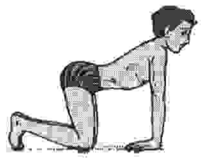
The picture is not yet complete. Certain physical properties show that rotation is not quite free : there is an energy barrier of about 3 kcal/mol.

(i) Most stable conformation of a person is *A* & *B*,*C*,*D* are different yoga pose.
Yoga pose *C* is Chakrasana and benefits are Strengthens back muscles, tones adrenals, helps kidneys, front part of the body is being stretch entirely, which is good for people who want to be more expressive as the openness in the heart may work on their heart chakra. Due to the stretch at the upper part of the abdomen muscles, it gives some pressure on the internal organs of the abdomen and therefore, increasing their efficiency

(A)

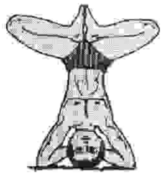


(B)



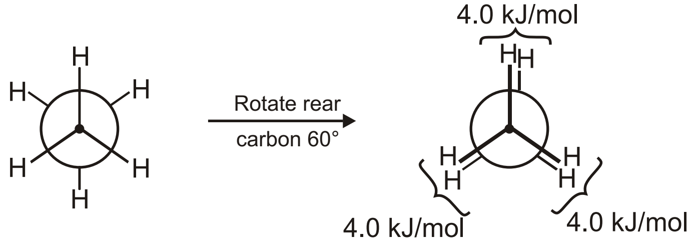
(C)

(D)



Energy

Despite what we've just said, we actually don't observe perfectly free rotation in ethane. Experiments show that there is a small (12 kJ/mol; 2.9 kcal/mol) barrier to rotation and that some conformations are more stable than others. The lowestenergy, most stable conformation is the one in which all six C—H bonds are as far away from one another as possible—staggered when viewed end-on in a Newman projection. The highest-energy, least stable conformation is the one in which the six C—H bonds are as close as possible—eclipsed in a Newman projection. At any given instant, about 99% of ethane molecules have an approximately staggered conformation and only about 1% are near the eclipsed conformation.



Ethane–staggered conformation

Ethane—eclipsed conformation

The extra 12 kJ/mol of energy present in the eclipsed conformation of ethane is called torsional strain. Its cause has been the subject of controversy, but the major factor is an interaction between C—H bonding orbitals on one carbon with antibonding orbitals on the adjacent carbon, which stabilizes the staggered conformation relative to the eclipsed one. Because the total strain of 12 kJ/mol arises from three equal hydrogen–hydrogen eclipsing interactions, we can assign a value of approximately 4.0 kJ/mol (1.0 kcal/mol) to each single interaction. The barrier to rotation that results can be represented on a graph of potential energy versus degree of rotation in which the angle between C—H bonds on front and back carbons as viewed end-on (the *dihedral angle*) goes full circle from 0 to 360°. Energy minima occur at staggered conformations, and energy maxima occur at eclipsed conformations, as shown.

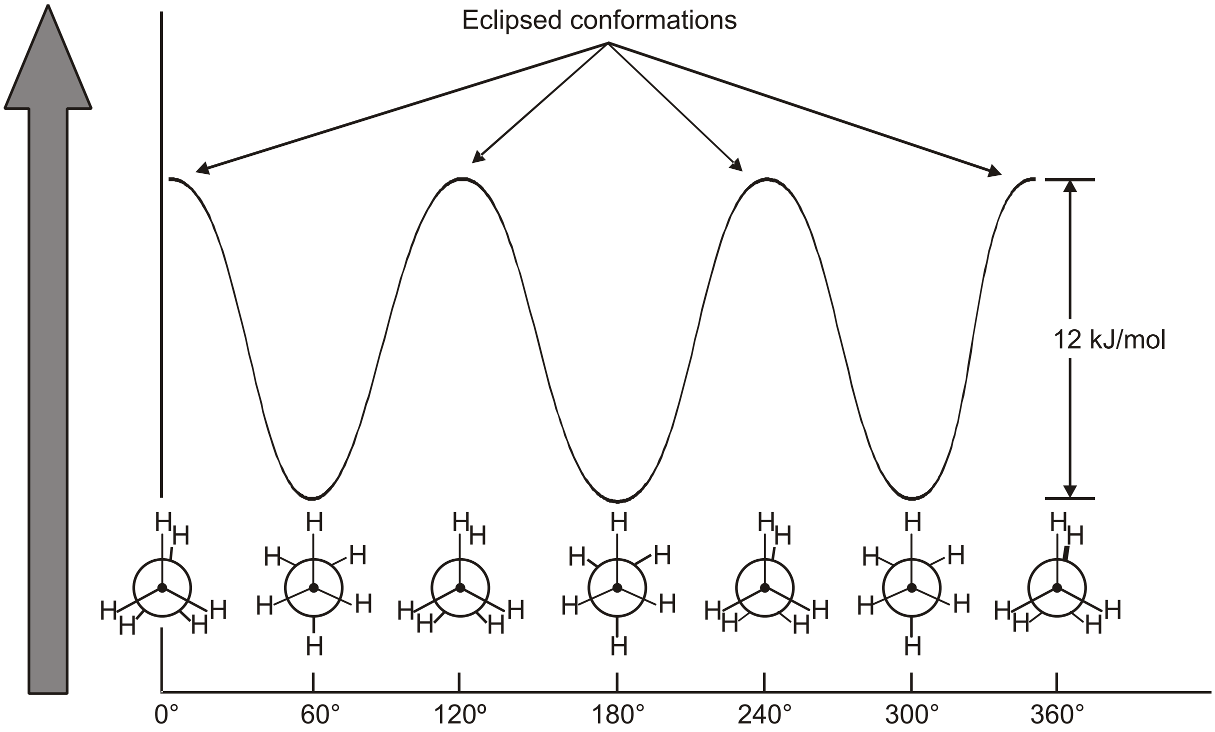


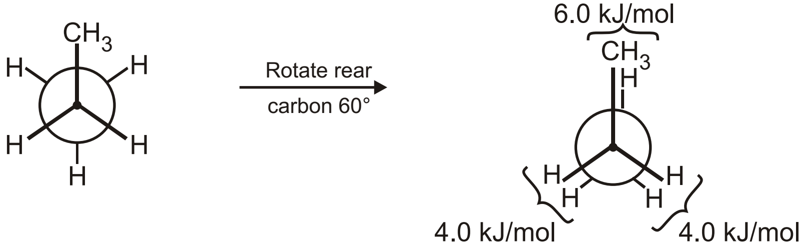
Fig. A graph of potential energy versus bond rotation in ethane.

The staggered conformations are 12 kJ/mol lower in energy than the eclipsed conformations.

CONFORMATION OF OTHER ALKANES

Propane, the next higher member in the alkane series, also has a torsional barrier that results in hindered rotation around the carbon–carbon bonds. The barrier is slightly higher in propane than in ethane — a total of 14 kJ/mol (3.4 kcal/mol) versus 12 kJ/mol.

The eclipsed conformation of propane has three interactions — two ethanetype hydrogen–hydrogen interactions and one additional hydrogen–methyl interaction. Since each eclipsing H H interaction is the same as that in ethane and thus has an energy "cost" of 4.0 kJ/mol, we can assign a value of 14 (2 4.0) 6.0k J/mol (1.4 kcal/mol) to the eclipsing H CH_3 interaction.

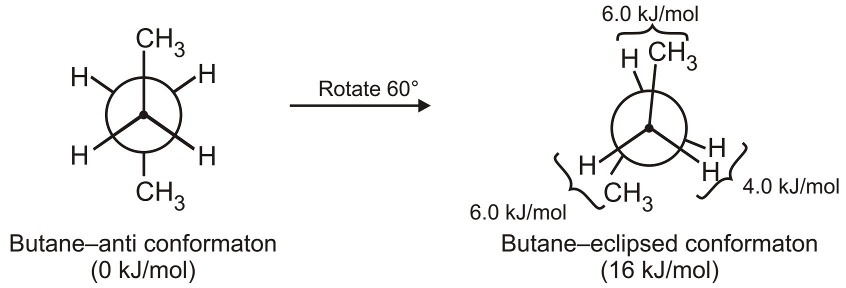


Staggered propane

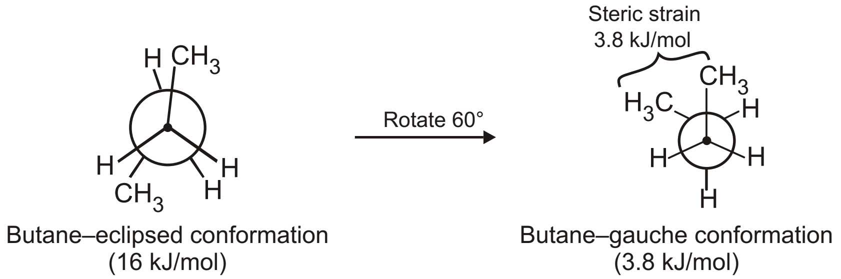
Eclipsed propane

Fig. Newman projections of propane showing staggered and eclipsed conformations. The staggered conformer is lower in energy by 14 kJ/mol.

The conformational situation becomes more complex for larger alkanes because not all staggered conformations have the same energy and not all eclipsed conformations have the same energy. In butane, for instance, the lowest-energy arrangement, called the anti conformation, is the one in which the two methyl groups are as far apart as possible — 180° away from each other. As rotation around the C2 — C3 bond occurs, an eclipsed conformation is reached in which there are two CH_3 H interactions and one H H interaction. Using the energy values derived previously from ethane and propane, this eclipsed conformation is more strained than the anti conformation by 2 × 6.0 kJ/mol + 4.0 kJ/mol (two CH_3 H interactions plus one H H interaction), for a total of 16 kJ/mol (3.8 kcal/mol).



As bond rotation continues, an energy minimum is reached at the staggered conformation where the methyl groups are 60° apart. Called the **gauche conformation**, it lies 3.8 kJ/mol (0.9 kcal/mol) higher in energy than the anti conformation even though it has no eclipsing interactions. This energy difference occurs because the hydrogen atoms of the methyl groups are near one another in the gauche conformation, resulting in what is called *steric strain*. **Steric strain** is the repulsive interaction that occurs when atoms are forced closer together than their atomic radii allow. It's the result of trying to force two atoms to occupy the same space.



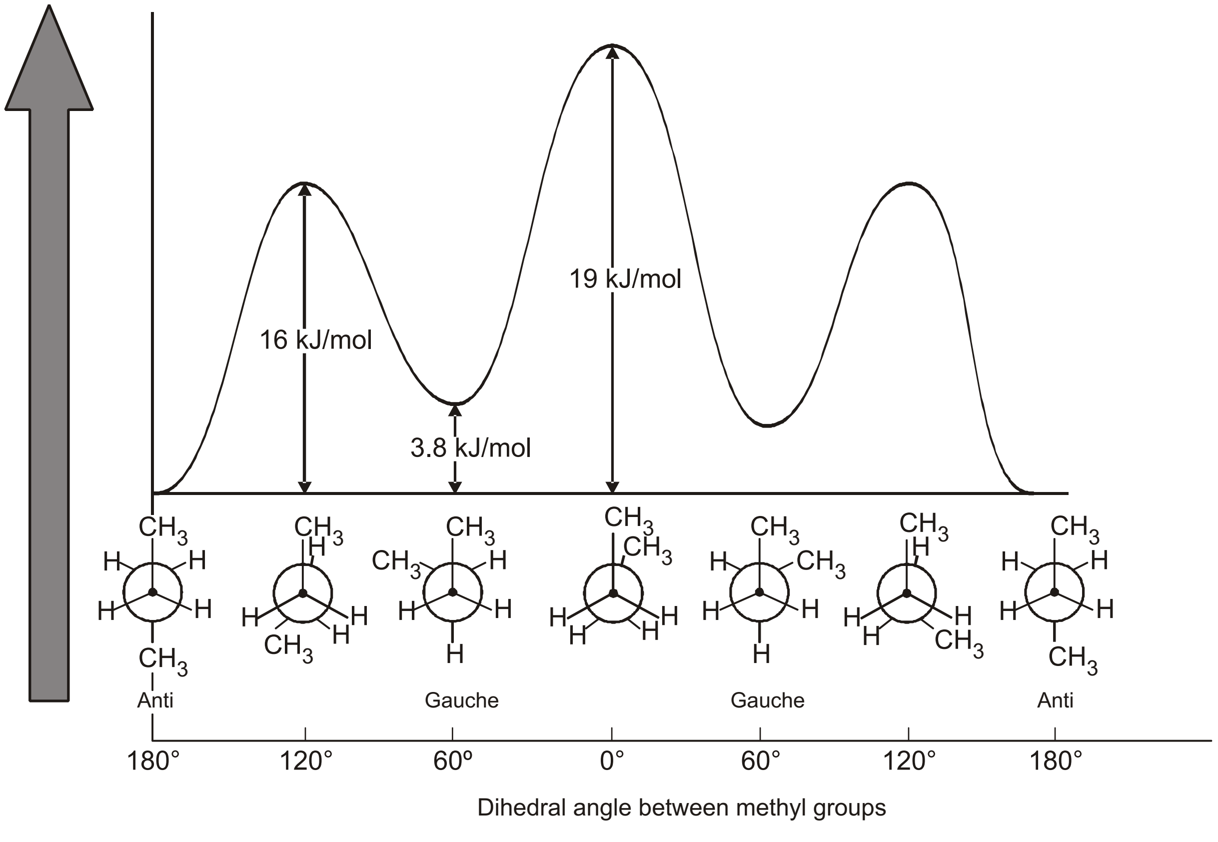
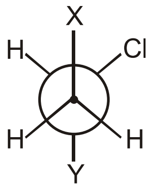


Fig. A plot of potential energy versus rotation for the C2—C3 bond in butane. The energy maximum occurs when the two methyl groups eclipse each other(fully eclipsed), and the energy minimum occurs when the two methyl groups are 180° apart (anti).

Table : Energy Costs for Interactions in Alkane Conformers

Interaction	Cause	Energy cost	
		(kJ/mol)	(kcal/mol)
H H eclipsed	Torsional strain	4.0	1.0
H CH_3 eclipsed	Mostly torsional strain	6.0	1.4
CH_3 CH_3 eclipsed	Torsional and steric strain	11	2.6
CH_3 CH_3 gauche	Steric strain	3.8	0.9

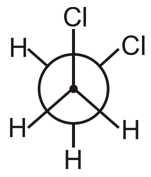
Solved Example



- In the Newman projection for 1, 2-dichloro propane *X* and *Y* can respectively be :
  (A) Cl and H
  (B) Cl and CH_3
  (C) CH_3 and Cl
  (D) H and CH_2Cl

Ans. (B, D)

Put the value of *X* and *Y* in each structure

(A)


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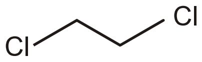

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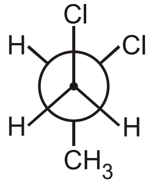

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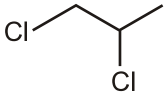
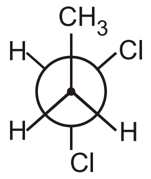


(C)


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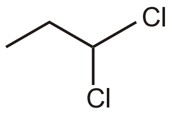
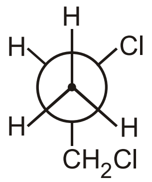


(D)


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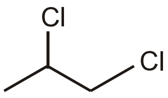
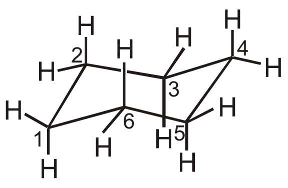
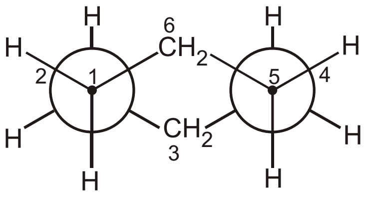


CONFORMATION OF CYCLOHEXANE

The cyclic compounds most commonly found in nature contain six-membered rings because six-membered rings can exist in a conformation that is almost completely free of strain. The conformation is called the **chair conformation.**



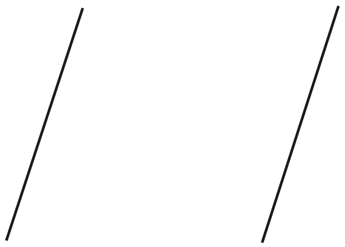
chair conformer of
cyclohexane



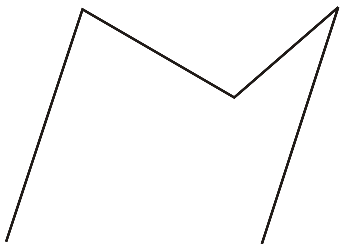
Newman projection of
the chair conformer

HOW TO DRAW CHAIR CONFORMER OF CYCLO HEXANE AND IDENTIFYING AXIAL AND EQUATORIAL BONDS

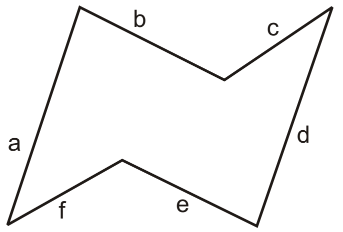
(1) Draw two parallel lines of same length, slanted upward and beginning at same level.



(2) Connect top-end by a V whose left hand side is greater than right hand side.

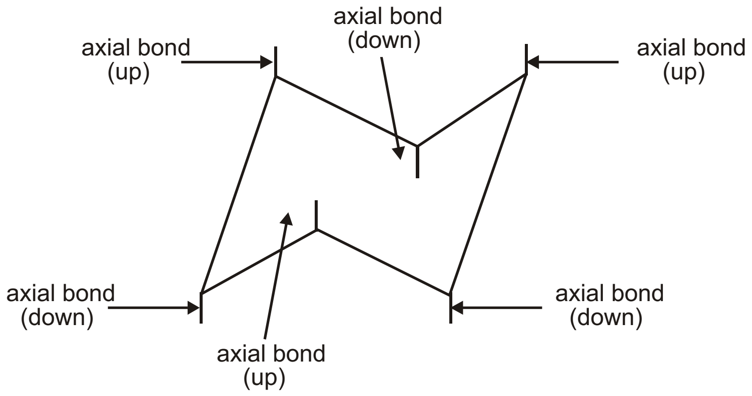


(3) Connect bottom end by an inverted V, whose L.H.S. is less than R.H.S.

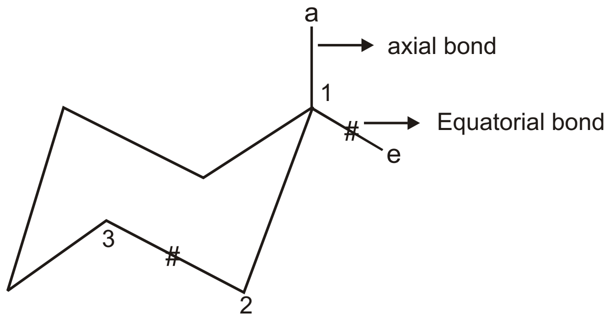


a||d (a is parallel to d)
b||e
c||f

(4) Axial bond are shown by vertical line and they are alternate above and below the ring.

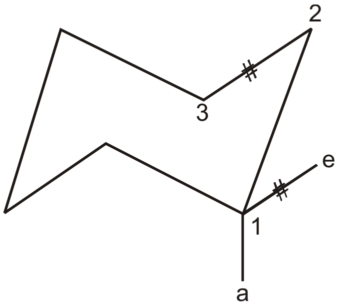


(5) If the axial bond is up then equatorial bond on the same carbon is on upward slant.

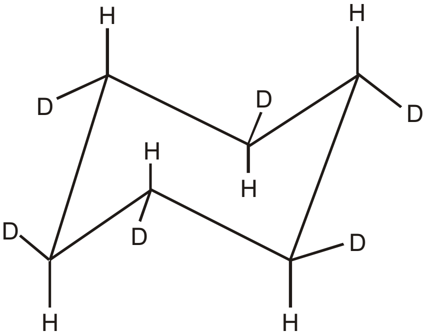


Equatorial bond is parallel to second carbon bond of the ring.

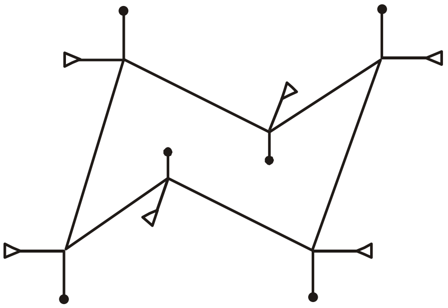
C_1 at equatorial is parallel to C_2 — C_3 bond of the ring.



Solved Example



H = Axial
D = Equatorial

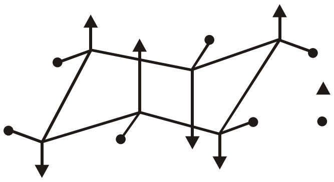


● = Axial
Δ = Equatorial

Solved Example

- Draw 1, 2, 3, 4, 5, 6-hexamethylcyclohexane with :
  (a) All the methyl groups in axial positions. (b) All the methyl groups in equatorial positions.

Ans. (a)

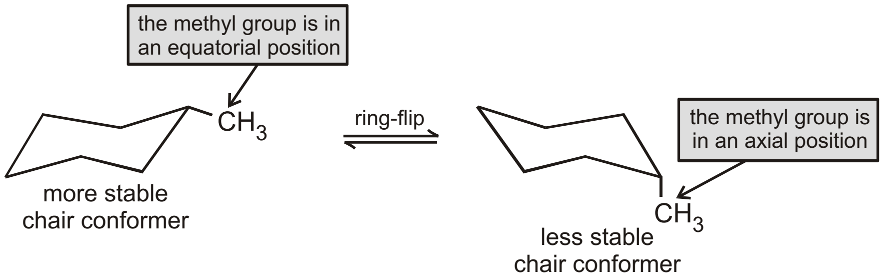


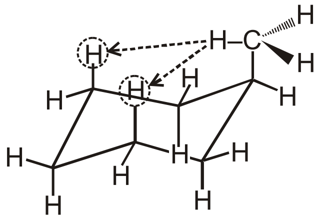
▲ = axial bond have $-CH_3$ groups
● = equatorial bond have –H-atom

(b) In above diagram of (a) ● = axial bond have $-CH_3$ groups
▲ = equatorial bond have –H-atom

CONFORMATIONS OF DISUBSTITUTED CYCLOHEXANES

A substituent is in the equatorial position in one chair conformer and in the axial position in the other chair conformer. The conformer with the substituent in the equatorial position is more stable, because in axial position group feels steric repulsion from hydrogen atom of the 3rd carbons of the ring it is known is **1,3-diaxial interactions (repulsion).**





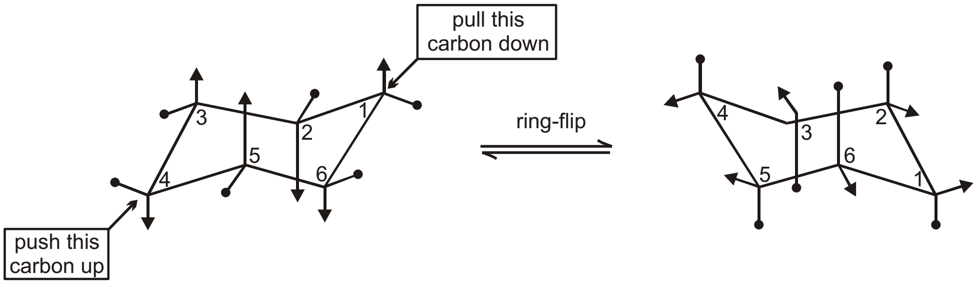
1,3-diaxial interactions

Ring Flip

In ring flip the bonds that are axial in one chair conformer are equatorial in the other chair conformer. The bonds that are equatorial in one chair conformer are axial in the other chair conformer.

- **During ring flip bonds that are equatorial in one chair conformer become axial in the other chair conformer.**

  As a result of the ease of rotation about its carbon-carbon single bonds, cyclohexane rapidly interconverts between two stable chair conformations. This interconversion is known as **ring-flip.** When the two chair conformers interconvert, bonds that are equatorial in one chair conformer become axial in the other chair conformer.



Solved Example

- The equilibrium constant for the ring-flip of fluorocyclohexane is 1.5 at 25ºC. Calculate the percentage of the axial conformer at the temperature.

Ans.

$$K_{eq} \quad \frac{[eq]}{ax} \quad 1.5$$

$$\%\ \text{axial} \quad \frac{[ax]}{[eq] \quad [ax]} \quad 100\%$$

$$\frac{[1]}{[1.5] \quad [1]} \quad 100\%$$

$$40\%$$

CONFORMATIONS OF DISUBSTITUTED CYCLOHEXANES

Monosubstituted cyclohexanes are always more stable with their substituent in an equatorial position, but the situation in disubstituted cyclohexanes is more complex because the steric effects of both substituents must be taken into account. All steric interactions in both possible chair conformations must be analyzed before deciding which conformation is favoured.

Let's look at 1,2-dimethylcyclohexane as an example. There are two isomers, cis-1,2-dimethylcyclohexane and trans-1,2-dimethylcyclohexane, which must be considered separately. In the cis isomer, both methyl groups are on the same face of the ring and the compound can exist in either of the two chair conformations shown.

cis-1,2-Dimethylcyclohexane

One gauche
interaction (3.8 kJ/mol)
Two $CH_3 \longleftrightarrow H$ diaxial
interactions (7.6 kJ/mol)
Total strain: 3.8 + 7.6 = 11.4 kJ/mol

One gauche
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Two $CH_3 \longleftrightarrow H$ diaxial
interactions (7.6 kJ/mol)
Total strain : 3.8 + 7.6 = 11.4 kJ/mol

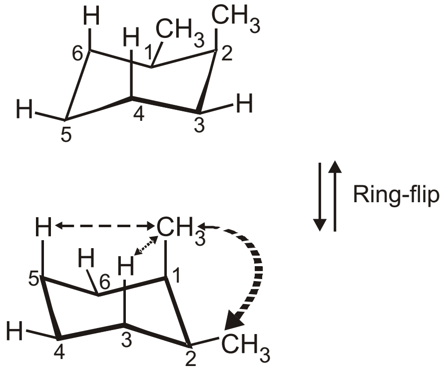


Figure 4.15 Conformations of cis-1,2-dimethylcyclohexane. The two chair conformations are equal in energy because each has one axial methyl group and one equatorial methyl group.

Both chair conformations of cis-1,2-dimethylcyclohexane have one axial methyl group and one equatorial methyl group. The top conformation in Figure 4.15 has an axial methyl group at C2, which has 1,3-diaxial interactions with hydrogens on C4 and C6. The ring-flipped conformation has an axial methyl group at C1, which has 1,3-diaxial interactions with hydrogens on C3 and C5. In addition, both conformations have gauche butane interactions between the two methyl groups. The two conformations are equal in energy, with a total steric strain of 3 3.8 kJ/mol = 11.4 kJ/mol (2.7 kcal/mol).

In trans-1, 2-dimethylcyclohexane, the two methyl groups are on opposite faces of the ring and the compound can exist in either of the two chair conformations. The situation here is quite different from that of the cis isomer. The top conformation in Figure 4.16 has both methyl groups equatorial and therefore has only a gauche butane interaction between them (3.8 kJ/mol) but no 1,3-diaxial interactions. The ring-flipped conformation, however, has both methyl groups axial. The axial methyl group at C1 interacts with axial hydrogens at C3 and C5, and the axial methyl group at C2 interacts with axial hydrogens at C4 and C6. These four 1,3-diaxial interactions produce a steric strain of 4 3.8 kJ/mol = 15.2 kJ/mol and make the diaxial conformation 15.2 – 3.8 = 11.4 kJ/mol less favourable than the diequatorial conformation. We therefore predict that trans-1,2-dimethylcyclohexane will exist almost exclusively in the diequatorial conformation.

trans-1,2-Dimethylcyclohexane

One gauche
interaction (3.8 kJ/mol)

Four $CH_3 \longleftrightarrow H$ diaxial
interactions (15.2 kJ/mol)

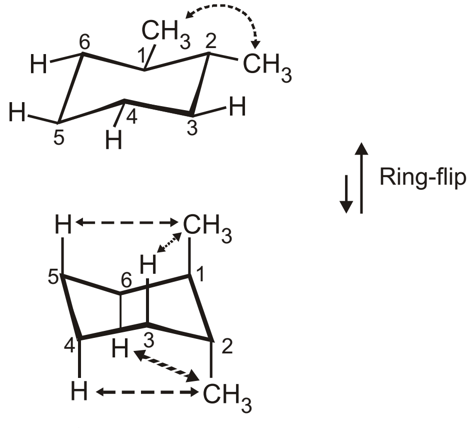


Figure 4.16 Conformations of trans-1,2-dimethylcyclohexane. The conformation with both methyl groups equatorial (top) is favored by 11.4 kJ/mol (2.7 kcal/mol) over the conformation with both methyl groups axial (bottom).

Solved Example

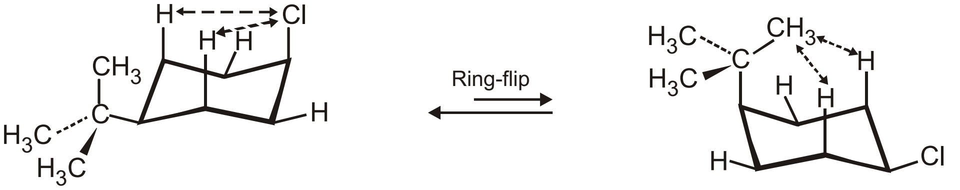
- **Drawing the Most Stable Conformation of a Substituted Cyclohexane**

  Draw the more stable chair conformation of cis-1-tert-butyl-4-chlorocyclohexane. By how much is it favored?

  Strategy

  Draw the two possible chair conformations, and calculate the strain energy in each. Remember that equatorial substituents cause less strain than axial substituents.

Sol. First draw the two chair conformations of the molecule :



2 × 1.0 = 2.0 kJ/mol steric strain

2 × 11.4 = 22.8 kJ/mol steric strain

Disubstituted Cyclohexane

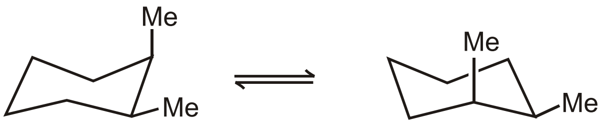
If 2 substituents are on cyclohexane the lowest energy conformation:

(a) Has both substituents equatorial (if possible)

(b) The group with the largest A value equatorial

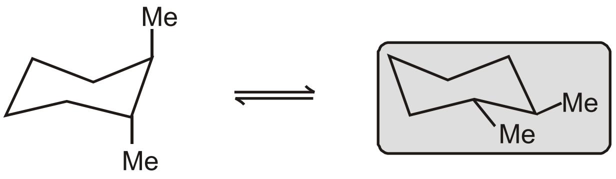
(c) t-Bu is NEVER axial

1,2-cis



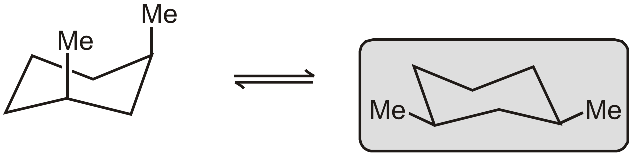
1 ax. 1 eq. versus 1ax. 1 eq.
same energy

1,2-trans



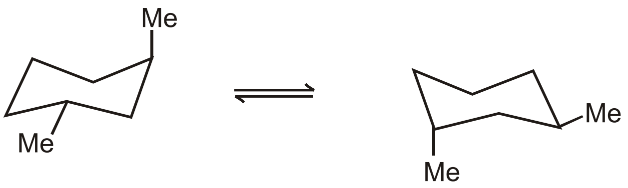
2 ax. versus 2 eq.
all equatorial preferred

1,3-cis



2 ax. versus 2 eq.
all equatorial preferred

1,3-trans

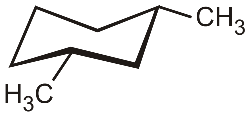


1 ax. 1 eq. versus 1ax. 1eq.
same energy

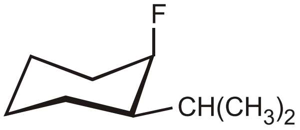
Solved Example

- Draw the ***lowest energy*** conformation adopted by each of the following molecules :

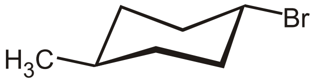
(a) ***cis***-1,3-Dimethylcyclohexane



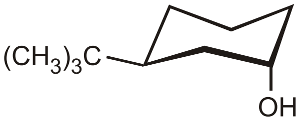
(b) ***cis***-1-Fluro-2-isopropylcyclohexane



(c) ***trans***-1-Bromo-4-methylcyclohexane

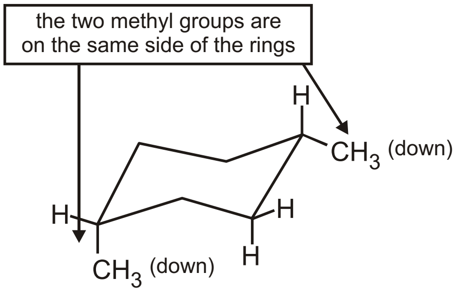


(d) ***trans***-3-tert-butylcyclohexanol

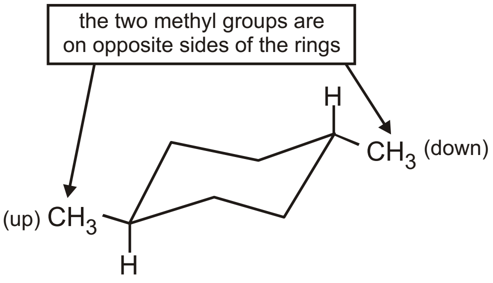


IDENTIFYING CIS & TRANS

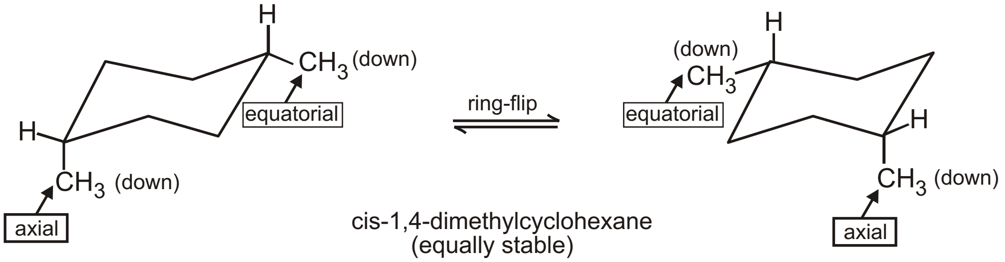
If there are two substituents on a cyclohexane ring, both substituents have to be taken into account when determining which of the two chair conformers is the more stable. Let's start by looking at 1,4-dimethylcyclohexane. First of all, there are two different dimethylcyclohexanes. One has both methyl substituents on the same side of the cyclohexane ring; it is the **cis isomer** (cis is Latin for ''on this side''). The other has the two methyl substituents on opposite sides of the ring; it is the **trans isomer** (trans is Latin for ''across''). cis-1,4-Dimethylcyclohexane and tran-1,4-dimethylcyclohexane are called **geometric isomers or cis-trans stereoisomers-**they have the same atoms, and the atoms are linked in the same order, but they differ in the spatial (stereo) arrangement of the atoms.



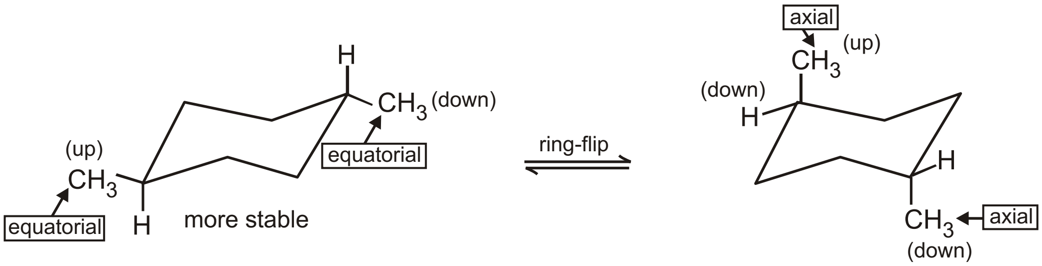
cis-1,4-dimethylcyclohexane



trans-1,4-dimethylcyclohexane



cis-1,4-dimethylcyclohexane
(equally stable)

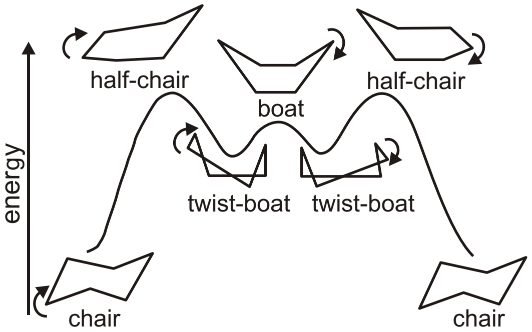


A summary of the various axial and equatorial relationships among substituent groups in the different possible cis and trans substitution patterns for disubstituted cyclohexanes is given in Table.

Table : Axial and Equatorial Relationships in Cis- and Trans-Disubstituted Cyclohexanes.

Cis/trans substitution pattern	Axial/equatorial relationships
1,2-Cis disubstituted	a, e or e, a
1,2-Trans disubstituted	a, a or e, e
1,3-Cis disubstituted	a, a or e, e
1,3-Trans disubstituted	a, e or e, a
1,4-Cis disubstituted	a, e or e, a
1,4-Trans disubstituted	a, e or e, e

Chair forms convert into various other forms(conformers *i.e.*, halfchair, twist boat and boat) during ringflip

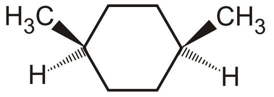


The boat conformer is further destabilized by the close proximity of the **flagpole hydrogens** which causes steric strain.

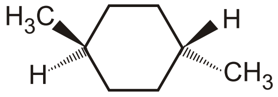
The twist-boat conformer is more stable than the boat conformer because the flagpole hydrogens have moved away from each other, thus reducing the steric strain somewhat.

Conformation Analysis of Disubstituted Cyclohexanes

We'll begin with cis- and trans-1,4-dimethylcyclohexane. A conventional method uses wedge and dash descriptions to represent cis and trans stereoisomers in cyclic systems.

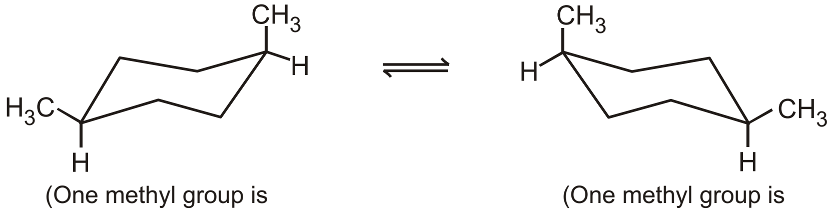


cis-1,4-Dimethylcyclohexane



trans-1,4-Dimethylcyclohexane

Each other by ring flipping. The equatorial methyl group becomes axial, and the axial methyl group becomes equatorial.

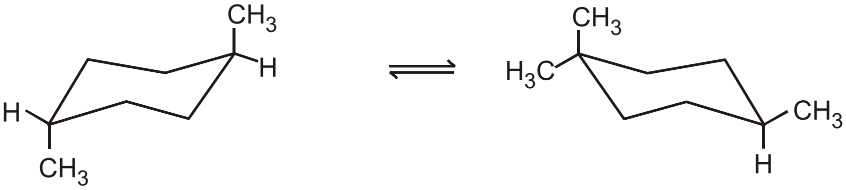


(One methyl group is axial, the other equatorial)

(One methyl group is axial, the other equatorial)

(Both methyl groups are up)
cis-1,4-Dimethylcyclohexane

The methyl groups are described as cis because both are up relative to the hydrogen present at each carbon. If both methyl groups were down, they would still be cis to each other. Notice that ring flipping does not alter the cis relationship between the methyl groups. Nor does it alter their up-versus-down quality; substituents that are up in one conformaion remain up in the ring-flipped form.



(Both methyl groups are axial: less stable chair conformation)

(Both methyl groups are equatorial: more stable chair conformation)

(One methyl group is up, the other down)
trans-1,4-Dimethylcyclohexane

The more stable chair-the one with both methyl groups equatorial is adopted by most of the trans-1,4-dimethylcyclohexane molecules.

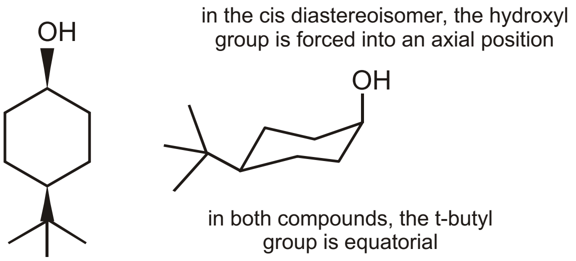
Trans-1,4-Dimethylcyclohexane is more stable than cis-1,4-dimethylcyclohexane because both of the methyl groups are equatorial in its most stable conformation. One methyl group must be axial in the cis stereoisomer.

☑ SPECIAL TOPIC

t-BUTYL GROUPS

We have already seen how a *t*-butyl group always prefers an equatorial position in a ring. This makes it very easy to decide which conformation the two different compounds below will adopt

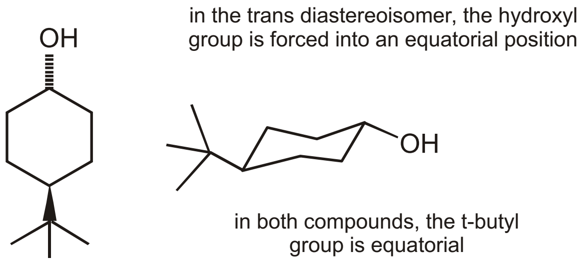
cis-4-t-butylcyclohexanol



in the cis diastereoisomer, the hydroxyl group is forced into an axial position

in both compounds, the t-butyl group is equatorial

trans-4-t-butylcyclohexanol

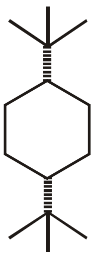


in the trans diastereoisomer, the hydroxyl group is forced into an equatorial position

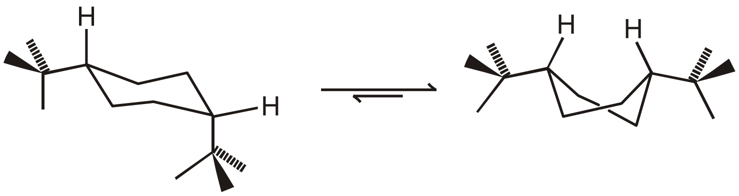
in both compounds, the t-butyl group is equatorial

Cis-1,4-di-t-butylcyclohexane

An axial *t*-butyl group really is very unfavourable. In cis-1,4-di-*t*-butylcyclohexane, one *t*-butyl group would be forced axial if the compound existed in a chair conformation. To avoid this, the compound prefers to pucker into a twist boat so that the two large groups can both be in equatorial positions (or 'pseudoequatorial', since this is not a chair).



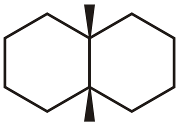
cis-1,4-di-t-butylcyclohexane



the twist-boat conformer (with both t-butyl groups in pseudoequatorial positions) is lower in energy than the chair conformer.

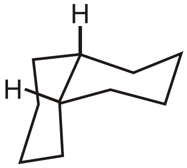
☑ SPECIAL TOPIC

1. Fused rings

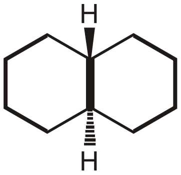


cis-decalin

≡

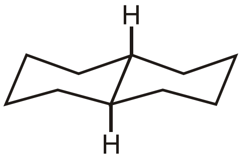


can ring flip



trans-decalin

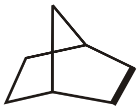
≡



cant' ring flip (locked)

bicyclo[4.4.0] decane

2. Bridged rings



conformationally locked

bicyclo[2.2.1] heptane

3. Spirocyclic rings (rare)

spiro[4.4] nonane

Conformation of cyclohexane

Cycloalkanes ring strain :

Compounds with three- and four-membered rings were not as stable as compounds with five or six-membered rings.

The German chemist Adolf von Baeyer first proposed in 1885 that the instability of three- and four-membered rings was due to angle strain. We know that an sp^3 hybridized carbon has ideal orbital angles of 109.5°. Baeyer suggested that the stability of a cycloalkane could be predicted by determining how close the bond angle of a planar cycloalkane is to the optimal tetrahedral bond angle of 109.5°. The angles in a regular triangle are 60°. The bond angles in cyclopropane, therefore, are compressed from the desired tetrahedral angle of 109.5° to 60°. The deviation of the bond angle from the desired bond angle causes the strain known as **angle strain.**

Cyclic compounds twist and bend in order to achieve a structure that minimizes the three different kinds of strain that can destabilize a cyclic compound.

(1) Angle strain is the strain induced in a molecule when the bond angles are different from the desired tetrahedral bond angle of 109.5°.

(2) Torsional strain is caused by repulsion of the bonding electrons of one substituent with the bonding electrons of a nearby substituent.

(3) Steric strain is caused by atoms or groups of atoms approaching each other too closely.

Solved Examples

- **Alkanes Stereochemistry**

(1) For the molecules below :

(a) Provide a 3 dimensional structure at the indicated atoms.

(b) Draw the Newman projection for your structure indicating the direction of sight with an arrow.

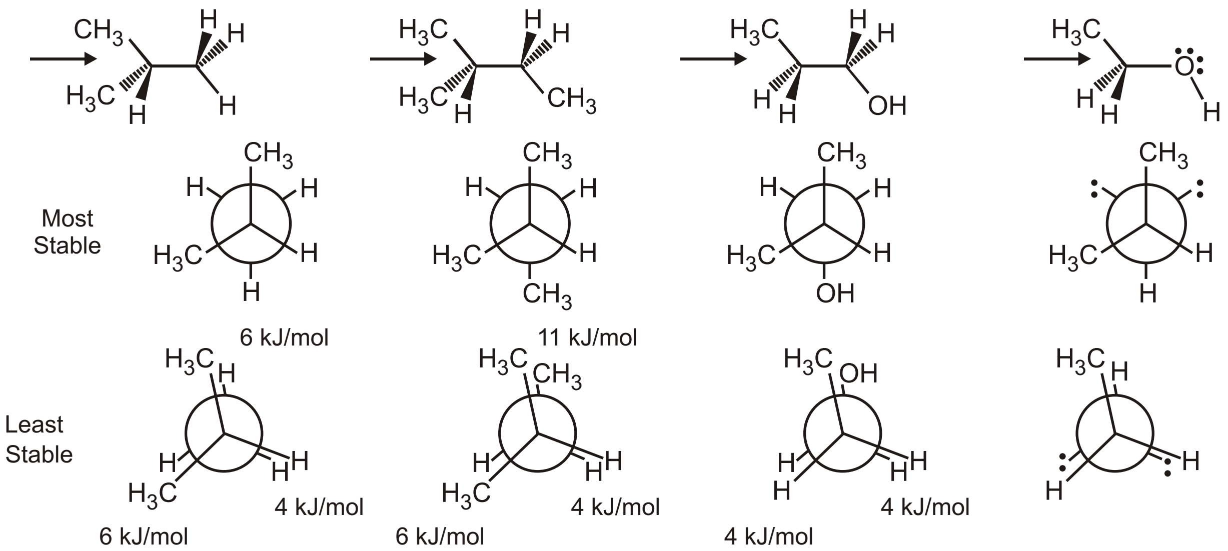
(c) Draw the Newman projection for the most stable conformation.

(d) Draw the Newman projection for the least stable conformation.

(e) If possible, calculate the energy difference between the most and least stable conformations.

$(H_3C)_2HC—CH_3$ $(H_3C)_2HC—CH_2CH_3$ $H_3CH_2C—CH_2OH$ $H_3CH_2C—OH$

barrier to rotation= 17kJ/mol(why?)

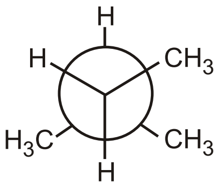


17 – 4 – 4 = 9 kJ/mol for each CH_3 : OH eclipse

EXERCISE

SINGLE CHOICE QUESTIONS

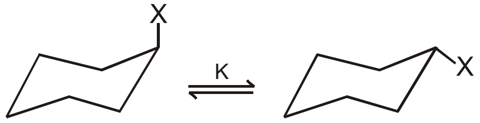
1. What compound is represented by the Newman projection shown?



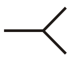
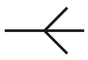
(A) $CH_3CH_2CH_3$ (B) $(CH_3)_2CHCH_2CH_3$

(C) $CH_3CH(CH_3)_2$ (D) $CH_3CH_2CH_2CH(CH_3)_2$

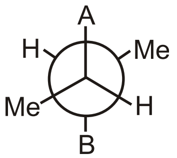
2.



K Equilibrium constant is maximum for

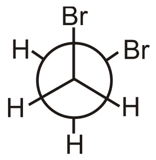
(A) –Me (B) –Et (C)  (D) 

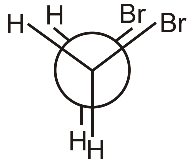
3. Identify (*A*) and (*B*) in Newman's projection of 2, 3-dimethyl pentane

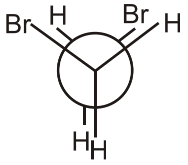


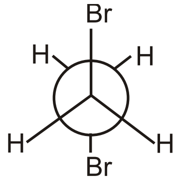
(A) $-CH_3, -CH_3$ (B) $-H, -C_2H_5$ (C) $-C_2H_5, -CH_3$ (D) $-C_2H_5, -C_2H_5$

4. Rank the following conformations in order of increasing energy

(I) 

(II) 

(III) 

(IV) 

(A) IV I III II (B) III II IV I

(C) II III I IV (D) IV III II I

5. Dipole moment of cis-1, 2-dichloro ethene is :

(A) 3 (B) $\sqrt{\ }$ (C) $\sqrt{3}$ (D) ^{2}

6. When methyl group is in axial position in methyl cyclohexane, the molecule has :

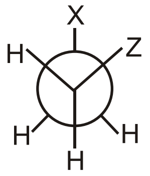
(A) One Gauche interaction (B) Two Gauche interaction

(C) No Gauche interection (D) Three Gauche interection

7. Bridge head hydrogen of the conformer of cis-decaline is positioned as :

(A) a, a (B) e, e (C) a, e (D) pseudo-a, pseudo-e

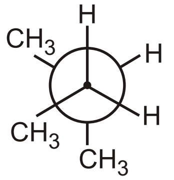
8. Gauche conformer is stable when

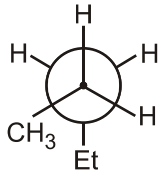


(A) $X \quad Z \quad -CH_3$ (B) $X \quad Z \quad -OH$

(C) $X \quad Z \quad -Br$ (D) $X \quad Z \quad -C_2H_5$

9.





Type of isomerism shown by given pairs is :

(A) conformatioinal (B) Positional

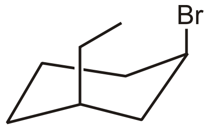
(C) Nuclear (D) Metamerism

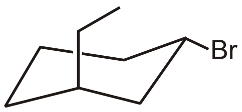
10. Isomers which can be interconverted through rotation around a single bond are :

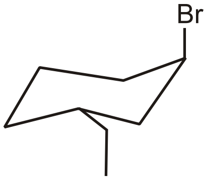
(A) conformers (B) diastereomers

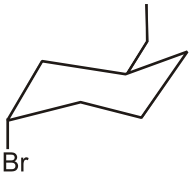
(C) enantiomers (D) positional isomers.

11. Which one of the following drawings shows trans-1-bromo-3-ethylcyclohexane in its highest energy conformation?

(A) 

(B) 

(C) 

(D) 

12. Which of the following best explains the relative stabilities of the eclipsed and staggered forms of ethane? The .... form has the most .... strain.

(A) eclipsed; steric (B) eclipsed; torsional

(C) staggered; steric (D) staggered; torsional

13. Which of the following statements about the conformers that result, from rotation about the C2-C3 bond of butane is correct?

(A) The highest energy conformer is one in which methyl groups are eclipsed by hydrogens

(B) The gauche conformer is an eclipsed one

(C) Steric strain is absent in the eclipsed forms

(D) Torsional strain is absent in the eclipsed forms

(E) none of the above

14. Which of the following correctly ranks the cycloalkanes in order of increasing ring strain per methylene?

(A) cyclopropane < cyclobutane < cyclohexane < cycloheptane

(B) cyclohexane < cycloheptane < cyclobutane < cyclopropane

(C) cycloheptane < cyclobutane < cyclopentane < cyclopropane

(D) cyclopentane < cyclopropane < cyclobutane < cyclohexane

(E) cyclopropane < cyclopentane < cyclobutane < cyclohexane

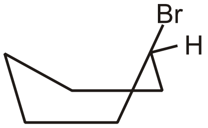
15. Which of the following correctly lists the conformations of cyclohexane in order of increasing energy ?

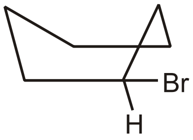
(A) chair < boat < twist-boat < half-chair (B) half-chair < boat < twist-boat < chair

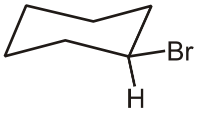
(C) chair < twist-boat < half-chair < boat (D) chair < twist-boat < boat < half-chair

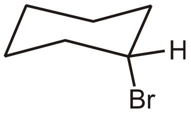
(E) half-chair < twist-boat < boat < chair

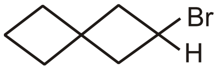
16. Which of the following is the most stable conformation of bromocyclohexane?

(I) 

(II) 

(III) 

(IV) 

(V) 

(A) I (B) II (C) III (D) IV

(E) V

17. In the boat conformation of cyclohexane, the “flagpole” hydrogens are located :

(A) on the same carbon (B) on adjacent carbons

(C) on C-1 and C-3 (D) on C-1 and C-4

(E) none of the above

MULTIPLE CHOICE QUESTIONS

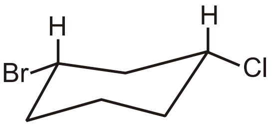
1. Twist boat conformer of cyclohexane is more stable than

(A) boat (B) half-chair (C) chair (D) All of these

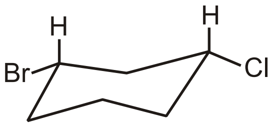
UNSOLVED EXAMPLE

1. Determine whether each of the following compounds is a cis isomer or a trans isomer.

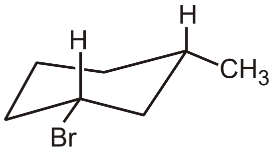
(a)



(b)



(c)



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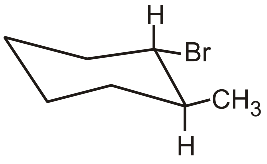
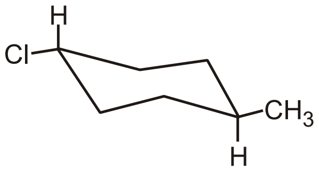
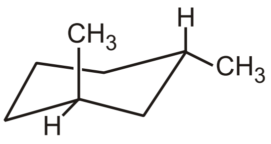


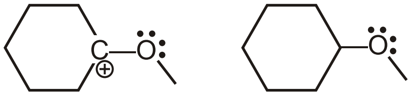
(e)



(f)



2. For the conformation of lowest energy estimate the atomic angles in the cation and the neutral molecule drawn below. Provide one number only for each question.



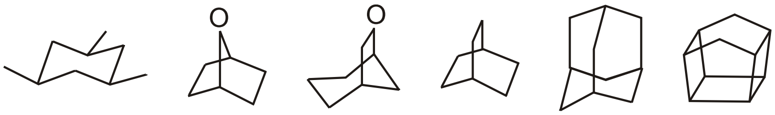
(a) C — O — C bond angle in cation.
(b) C — O — C bond angle in neutral molecule.
(c) C — O — C — C dihedral angle in the cation
(d) C — O — C — C dihedral angle in the neutral molecule.

3. (a) Draw a chair cyclohexane and put in all the axial bonds.
(b) On a second chair cyclohexane. put in all the equatorial bonds.
(c) Draw a cyclohexane with a bromine in an equtorial position.
(d) Draw a cyclohexane with a bromine in an axial position.

4. Draw both possible conformations for the indicated cyclohexane :
(a) trans -1-chloro-2-methylcyclohexane.
(b) cis-1-chloro-2-methylcyclohexane
(c) trans-1-chloro-3-methylcyclohexane
(g) a cyclohexane with 2 methyl groups, both axial.
(d) cis-1-chloro-3-methylcyclohexane
(e) trans-1-chloro-4-methylcyclohexane.
(f) cis-1-chloro-4-methylcyclohexane
(h) a cyclohexane with 2 methyl groups, both equatorial.

SUBJECTIVE TYPE QUESTIONS

1. Identify the chair or boat six-membered rings in the following structures and say why that particular shape is adopted.



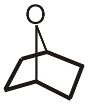
Purpose of the problem

Simple examples of chair and boat forms.

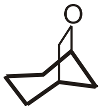
Suggested solution

The first three are relatively simple

simple chair
with all
substituents
equatorial

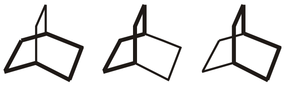


boat in cage
molecule with
no choice :
chair impossible

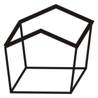


chair in cage
molecule with
some choice :
C* can move

The next two have several rings each, all boat in the first. We shall link that to the sixth molecule as it also has a boat and neither of these cage structures has any choice.

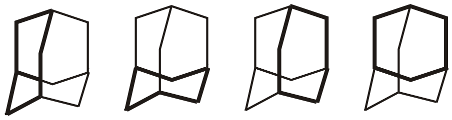


three boats
cage compound
has no choice



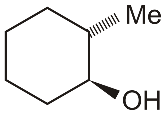
one boat
cage compound
has no choice

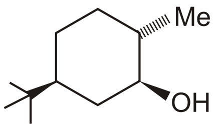
The rings are all chairs in the fifth molecule adamantane – a tiny fragment of a diamond molecule. The rings don't all look very chair-like in these diagrams – making a model of adamantane is the only way to appreciate this beautiful and symmetrical structure and to see all the chairs.

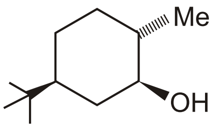


adamantane :
four chairs cage
compound has no
choice

2. Draw clear conformational drawings for these molecules, labelling each substituent as axial or equatorial.





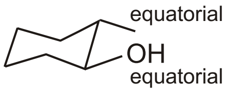


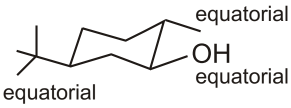
Purpose of the problem

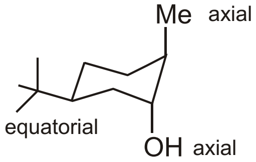
Simple practice at drawing chair cyclohexanes with axial and equatorial substituents.

Suggested solution

Your drawings may look different from ours but make sure the rings have parallel sides and don't ‘climb upstairs’. Make sure that the axial bonds are vertical and the equatorial bonds parallel to the next-ring-bond-but-one. The first molecule has a free choice so it puts both substituents equatorial. The last two molecules are dominated by the *t*-butyl groups, which insist on being equatorial.







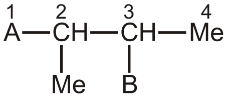
3. Contrary to $ClCH_2 — CH_2Cl$, in $FCH_2 — CH_2F$ gauche conformer is the more stable conformer. Explain this fact.

4. (a) What is 'gauche effect' ? Give examples.
(b) Draw the eclipsed and bisecting conformations of propylene (propene)

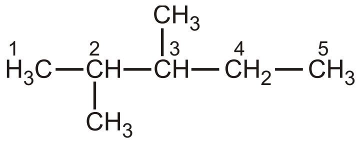
Answers

Single Choice Questions

1. (B) **2.** (D) **3.** (C) **4.** (A) **5.** (C) **6.** (A) **7.** (D) **8.** (B)
9. (B) **10.** (A) **11.** (B) **12.** (B) **13.** (E) **14.** (B) **15.** (D) **16.** (C)
17. (D)

3. 

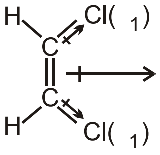
$$\overset{1}{A}—\underset{Me}{\overset{2}{C}H}—\underset{B}{\overset{3}{C}H}—\overset{4}{Me}$$



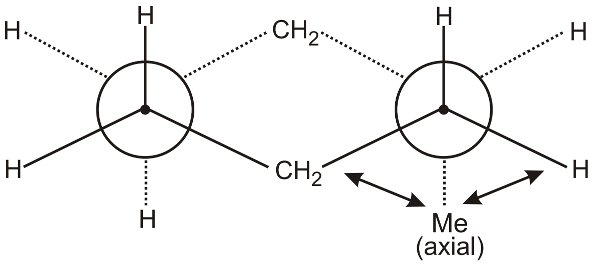
$$\overset{1}{H_3C}—\underset{CH_3}{\overset{2}{C}H}—\overset{CH_3}{\overset{3}{C}H}—\overset{4}{CH_2}—\overset{5}{CH_3}$$

One of the combinations is (A) – C_2H_5, (B) – CH_3

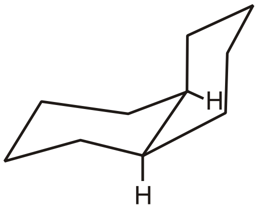
4. Order of increasing energy : Anti < Gauche < Partially eclipsed < Fully eclipsed.

5. 

$\sqrt{{}^{2}_{1}\quad {}^{2}_{1}\quad 2\quad {}_{1}\,{}_{1}\cos 60}$ $\sqrt{2\,{}^{2}_{1}\quad 2\quad {}_{1}\,{}_{1}\quad \frac{1}{2}}$ $\sqrt{3\quad {}^{2}}$ $\sqrt{3}$

6. 

one-n-butane gauch interaction

7. 

Bridge head hydrogen are pseudo a & pseudo e.

because this (H) are axial for 1 ring & equatorial for other thing.

Multiple Choice Questions

1. (A, B)

Stability order

Half chair < Boat < Twist boat < Chair

Unsolved Example

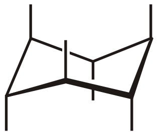
1. (a) = cis ; (b) = trans ; (c) = cis ; (d) = trans ;

(e) = trans ; (f) = trans.

2. (a) 120º (b) 108º - 110º (c) 0º or 180º (d) 60º

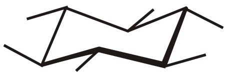
HINT : ***The last two questions might be assisted by some Newman Projections.***

3. (a)



axial bonds

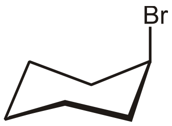
(b)



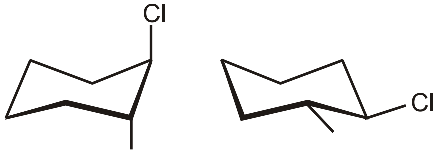
equatorial bonds

(c)

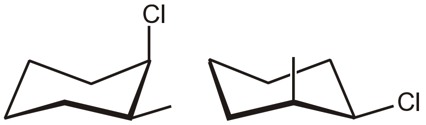
(d)



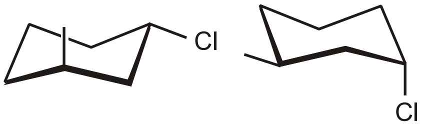
4. (a)



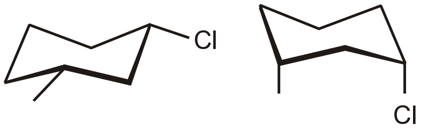
(b)



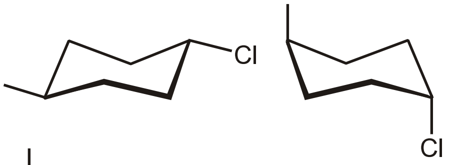
(c)



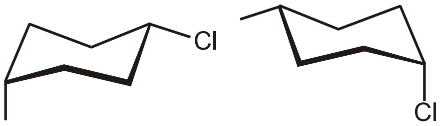
(d)



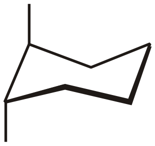
(e)



(f)

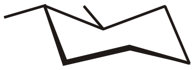


(g)



one possible answer

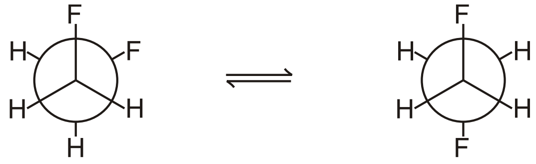
(h)



one possible answer

Subjective Type Questions

3. The situation in FCH_2CH_2F is found to be quite different from either $ClCH_2CH_2Cl$ or $BrCH_2CH_2Br$ in the fact that gauche conformer is found to more stable than the anti conformer, even in gaseous state. Different explanations have been offered for this unusual stability of gauche conformer over the anti form

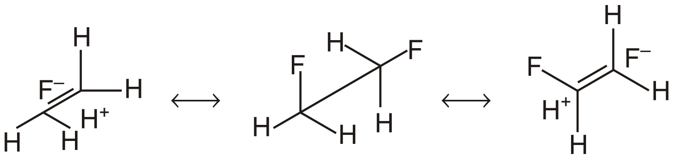


gauche-form (more stable) anti-form (Less stable)

Allinger *et al.* (1977) has explained the stability of gauche form on the basis of hyperconjugative interaction of the type, which is initiated by the high electronegativity of fluorine atom.

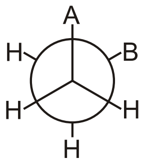
$F — CH_2 — CH_2 — F$ F — CH CH — FH H F — CH CH_2F

In order to involve both fluorine atom simultaneously in this interaction, the two C — F bonds must be orthogonal.

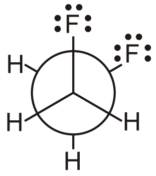


Small size of fluorine atom minimizes the van der Waals repulsive interaction in gauche conformer. Another explanation for preferred gauche conformation in the case of FCH_2CH_2F is the so called gauche effect a chain segment *A* – *B* – *C* – *D* will prefer gauche conformation when *A* and *D* are highly electronegative relative to *B* and *C* or *A* and *D* are themselves unshared electron pairs. In this case *A* and *D* are fluorine atom of high electronegativity.

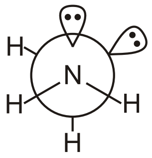
4. (a) In a conformational array, where *A* and *B* are second-row electronegative atoms such as *N*, *O*, or *F*, or unshared electron pair, the often observed preference for the gauche conformation (skew position) of *A* and *B* is called the 'gauche effect'. A few examples are given here.



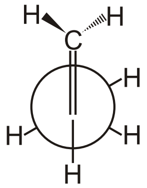
'gauche effect'



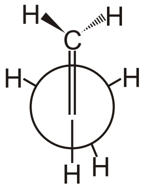
Preferred conformation of FCH_2CH_2F due to gauche effect



Preferred conformation of H_2NNH_2 due to gauche effect



Eclipsed conformation



Bisecting conformation

❑❑❑