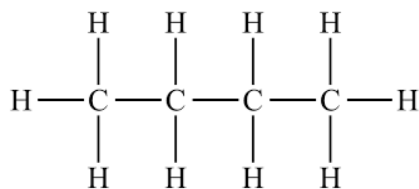


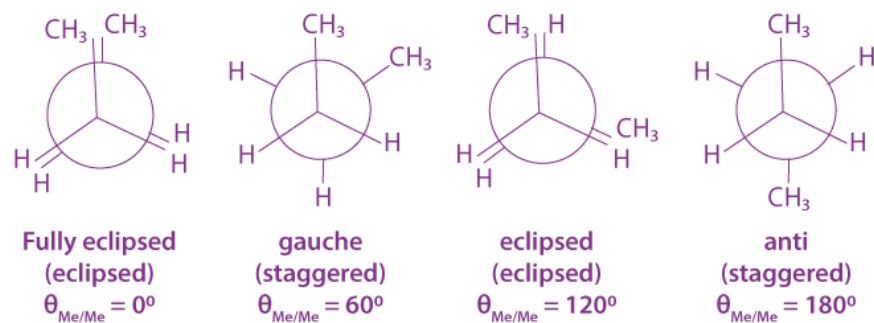
GEOMETRICAL ISOMERISM

CONFORMATIONAL ISOMERISM OF N-BUTANE.

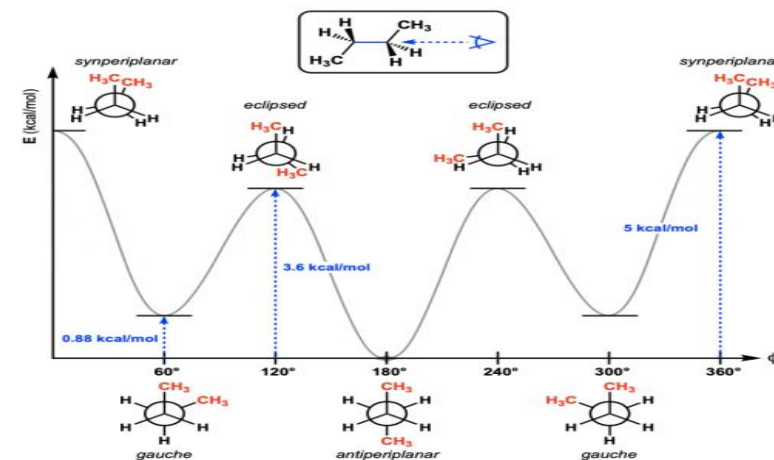


In butane there are two large methyl group attach to the centre two carbon the presence of 2 methyl group gives rise two types of staggered conformation that differ in the position of methyl group.

The staggered conformation in which the methyl group are exactly opposite to each others at an angle 180° between them called antistaggered conformation. The methyl group are staggered with each other or are closer called Gauch staggered conformation.



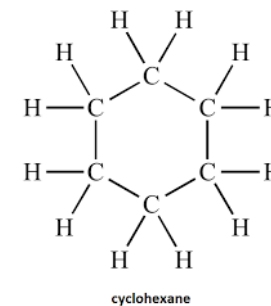
ENERGY DIAGRAM :-



The two larger group (bulky) required more energy to push together so eclipsed conformation required to 4 to 6 kcal/mole energy. So it is less stable antistaggered conformation are more stable because two methyl group are apt from each other required less energy.

The energy diagram shows energy different between various conformation of butane.

CONFORMATIONAL ISOMERISM OF CYCLOHEXANE :-

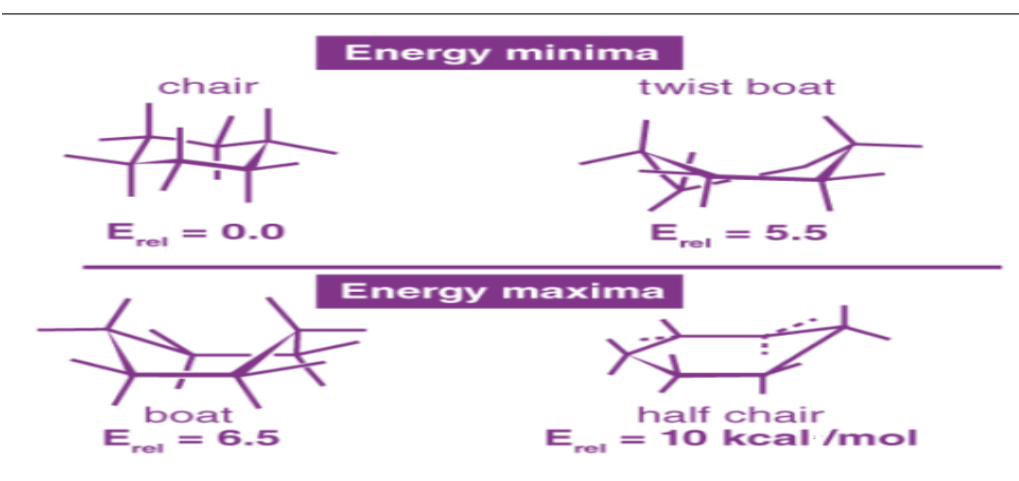


A regular hexagon shape contains internal angles of 120° . However, the carbon-carbon bonds belonging to the cyclohexane ring have a tetrahedral symmetry, with the bond angles corresponding to 109.5° .

This is the reason why the cyclohexane ring has a tendency to take up several warped conformations (so that the bond angles are brought closer to the tetrahedral angle (109.5°) and there is reduced overall strain energy).

Examples of common conformations of cyclohexane include the boat, the twist-boat, the chair, and the half-chair conformations, which are named based on the shape that the cyclohexane molecule assumes in them.

These four cyclohexane conformations have been illustrated below along with some insight into their stability.



It can be noted that the cyclohexane molecule has the ability to switch between the conformations listed above and that only the chair and the twist-boat conformations can be isolated into their respective pure forms.

Due to hydrogen-hydrogen interactions in these conformations, the bond length and the bond angle vary slightly from their nominal values.

The chair conformations of cyclohexane have lower energies than the boat forms. However, the rather unstable boat forms of cyclohexane undergo rapid deformation to give twist-boat forms which are the local minima corresponding to the total energy.

The hydrogen atoms belonging to the carbon-hydrogen bonds that are at a perpendicular angle to the mean plane are called axial hydrogens, whereas those belonging to the carbon-hydrogen bonds which are parallel to the mean plane are called equatorial hydrogens. These bonds are also referred to as axial and equatorial bonds respectively.

Boat And Chair Forms Of Cyclohexane :-

Cyclohexane is the most widely occurring ring in compounds of natural origin. Its prevalence, undoubtedly a consequence of its stability, makes it the most important of the cycloalkanes. The deviation of bond angle in cyclohexane molecules is more than in cyclopentane, it should be more strained and less reactive than cyclopentane. But actually, it is less strained and more stable than cyclopentane.

In order to avoid the strain, cyclohexane does not exist as a planar molecule as expected. It exists as a puckered ring which is non-planar and the bond angles are

close to tetrahedral bond angles. Two such puckered rings for cyclohexane are called the boat and chair conformations.

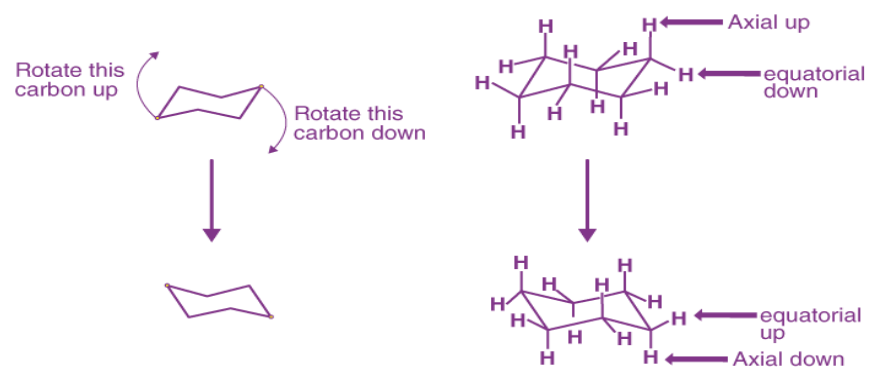
Stability of conformations of cyclohexane :-

Generally, in the chair-shaped conformation of cyclohexane, there are two carbon-hydrogen bonds of each of the following types:

- Axial 'up'
- Axial 'down'
- Equatorial 'up'
- Equatorial 'down'

This geometry of chair cyclohexane conformations is generally preserved when the hydrogen atoms are replaced by halogen atoms such as fluorine, chlorine, bromine, and iodine. The phenomenon wherein the cyclohexane molecule undergoes a conversion from one chair form to a different chair form is called chair flipping (or ring flipping).

An illustration detailing chair flipping is provided below.



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When chair flipping occurs, axial carbon-hydrogen bonds become equatorial and the equatorial carbon-hydrogen bonds become axial. However, they retain the corresponding 'up' or 'down' positions.

It can be noted that at a temperature of 25° Celsius, 99.99% of the molecules belonging to a given cyclohexane solution would correspond to a chair-type conformation.

The boat conformation of cyclohexane is not a very stable form due to the torsional strain applied to the cyclohexane molecule. The stability of this form is further affected by steric interactions between the hydrogen atoms. Owing to these factors, these conformations are generally converted into twist-boat forms which have a lower torsional strain and steric strain in them.

These twist-boat conformations of cyclohexane are much more stable than their boat-shaped counterparts. This conformation has a concentration of less than 1% in a solution of cyclohexane at 25°. In order to increase the concentration of this conformation, the cyclohexane solution must be heated to 1073K and then cooled to 40K.

Stereoisomerism in biphenyl compounds :-

Biphenyl is an aromatic hydrocarbon with a molecular formula $(C_6H_5)_2$, consists of two connected phenyl ring. Due to lack of formation of groups, it is unreactive in nature. (The two phenyl groups are linked by a single bond sp^2 known as pivotal bond).

Biphenyl does not show geometrical isomerism, its show conformational isomerism due to rotation around the single bond. Biphenyl containing for a large group in the

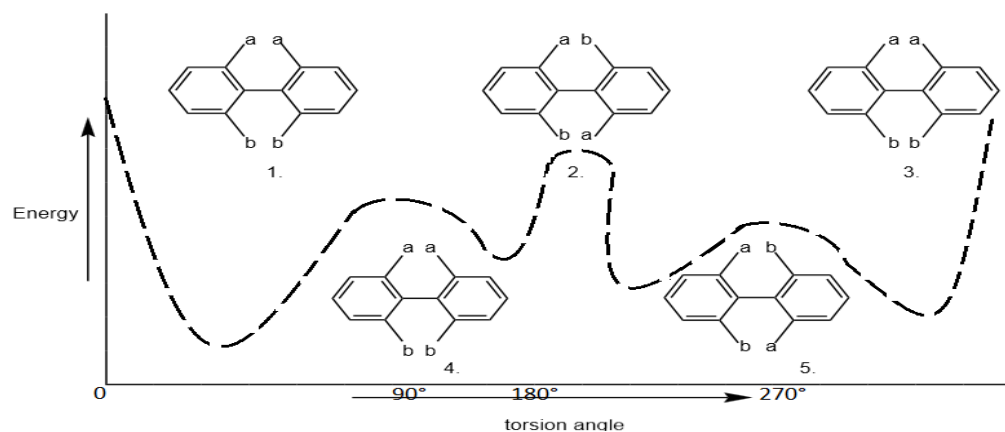
two ortho positions cannot freely rotate. Two ortho positions can free rotate about central bond because of strict hindrance plane. In such compounds, the two rings are in perpendicular plane.

The distance between two o-hydrogen in adjacent rings in the planar conformation is significantly in greater than twice the Vander wall's radius of hydrogen. The distance between two o-hydrogen is approx. 2.9\AA and the radius of Vander walls of hydrogen is approx. 2.4\AA due to this reason the rotation around the pivotal bond is not hampered by steric factor.

The diagram shows a 360° rotation around the pivotal bond. The inter-ring resonance or the energy of the compound is lowest at 90° angle therefore, when the torsion angle is 90° & 270° as shown in the figure.

The compound will have least energy & will be more stable thus the preferred conformation of the enantiomers is those in which the two phenyl planes are approximately but not exactly perpendicular to each other. Hence, the compound in the form of structure 3 & 4 will be more stable than in the form of structure 1, 2 & 4). In these structure (1, 2 & 5) the inter atomic distance between atoms a-a & b-b and a-b is minimum inter atomic distance.

The strict hindrance or repulsion will be greater than those of between atoms of structure 3 & 4. Thus, the structure (1, 2, 5) will have greater energy than that the



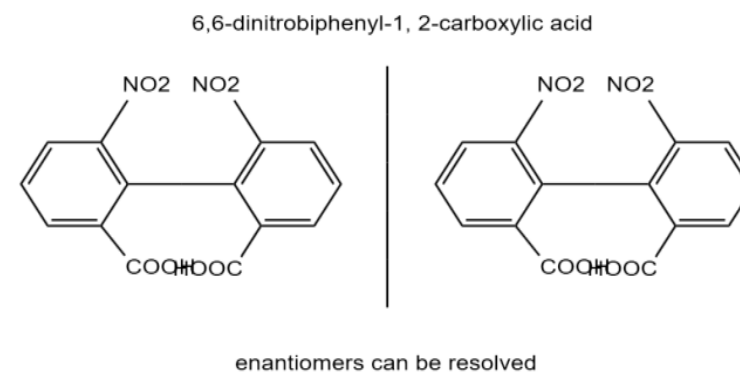
structure (3 & 4) & therefore, the structure (1, 2, 5) will be stable than that of structure (3 & 4).

If the energy barrier exceeds 80-100 KJ/mol, the stereoisomers can be repeated at normal room temperature because of their greater energy difference. Such isomerism which results due to restricted rotation around a single bond is termed as atropisomeric & the isomers are known as atropisomeric.

The term atropisomeric comes from a Greek word in which 'a' mean 'not' & 'tropes' means 'turn'. It means those compounds which resist turning around a single bond. The atropisomeric can be defined as isomers that can be isolated due to prevention or restriction of rotation about a given single bond usually between two planar molecules.

Biphenyl substituted on o-position become inclined to each other in respect of steric repulsion or hindrance among the atoms attached in the o-position, the pivotal bond is restricted. The interconversion between the two isomer is restricted. Therefore, the two isomers exist as separate entities & can be resolved to separate enantiomers. Stereoisomerism in biphenyl compounds .

Condition for biphenyl compounds to exhibit optical activity :-



1. There should be any functional group/atom at ortho position of rings. (Substitution at ortho position with large size such as – Cl, Br, I, COOH, NO₂, SO₃H, CH₃).
2. Each ring must be resolvable for that a is not equal b and c is not equal d.
3. This order is corresponds roughly to the order of Vander wall's radii of the group.
4. The biphenyl compounds containing large substituent or groups can be readily racemized in heating & separate into the form of enantiomer.

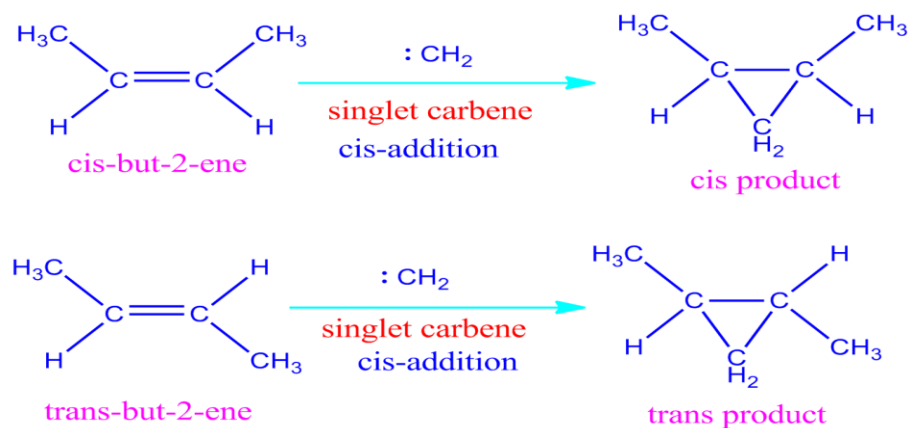
Stereospecific and stereoselective reactions :-

Stereoselectivity :-

The preferential formation of one stereoisomer over another in a chemical reaction. If the stereoisomers are enantiomers, one speaks of enantioselectivity (quantified by ee); if they are diastereomers, one speaks of diastereoselectivity.

Stereospecific :-

A reaction is termed stereospecific if, in such a reaction, starting materials differ only in their configuration are converted to stereoisomerically distinct products. According to this definition, a stereospecific process is necessarily stereoselective, but stereoselectivity does not necessarily imply stereospecificity.



Stereoselectivity :-

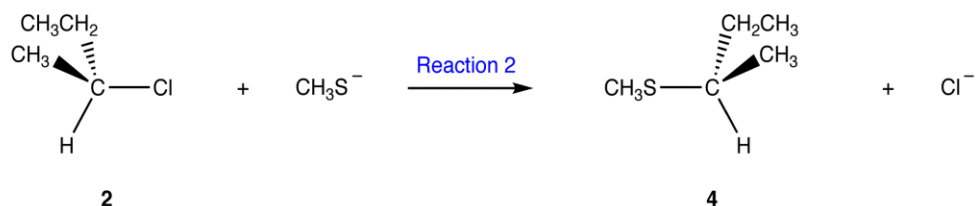
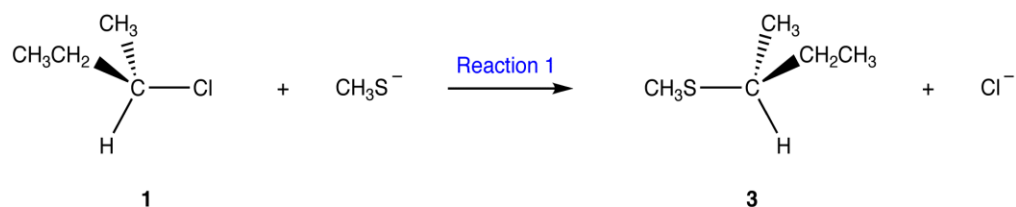
A stereoselective reaction is one in which a single reactant can give two or more stereoisomeric products, and one or more of these products is preferred over the others – even if the preference is very small.

Stereospecific :-

In a stereospecific reaction, one stereoisomer of the reactant gives one stereoisomer of the product, while a different stereoisomer of the reactant gives a different stereoisomer of the product.

Steps:

1. Look at your reaction.
2. If multiple stereoisomeric products are possible, but one is produced in excess, the reaction is stereoselective.
3. Consider the stereochemical features of the reactants to determine stereospecificity or lack thereof.
 - If another stereoisomer of the reactant will give identical products in identical ratios, then the reaction is not stereospecific.
 - If a different stereoisomer of the reactant or reagent gives a stereoisomerically different product, then the reaction is stereospecific.



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