



## STEREOCHEMISTRY – II

### CONFORMATIONAL ANALYSIS

So far, all stereoisomers discussed differ in configuration but a separate class of stereoisomers also exist which are called conformational isomers. The difference between them being that in a set of conformational isomers, the isomers can be converted from one isomer to the other by mere rotation of bonds. On the other hand, configurational isomers cannot be achieved in this fashion. A bond needs to be broken and reconnected at the same stereocentre in a different spatial arrangement to obtain a configurational isomer from another. As an example, the molecule of ethane is to be considered. Now, it cannot possibly have any configurational isomers since none of the carbons are dissymmetric. However, it may have conformational isomers. The atoms remain connected in the same order during conformational change. If the C1-C2-bond is considered in ethane, then it is possible to draw two structures, one in which the hydrogen atoms on one of carbon atoms eclipse the other and another where they are as far away from each other as possible. There is a difference in energy between the two structures. The eclipsed form has a higher potential energy than the staggered form (12 kJ mol<sup>-1</sup>) (Figure ).

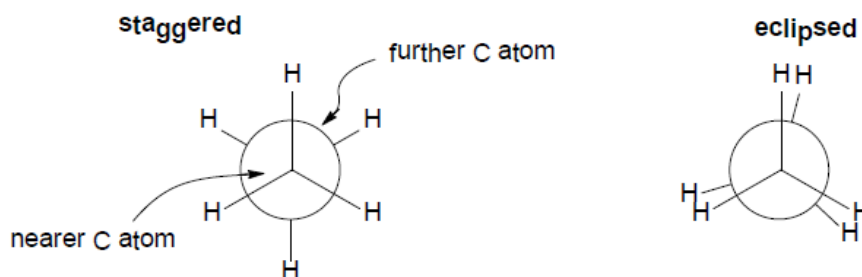
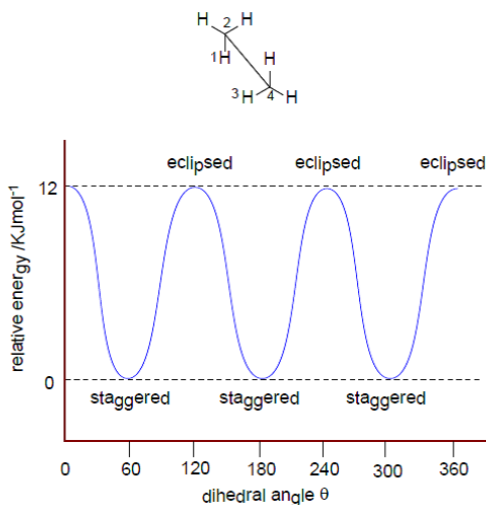


Figure 1

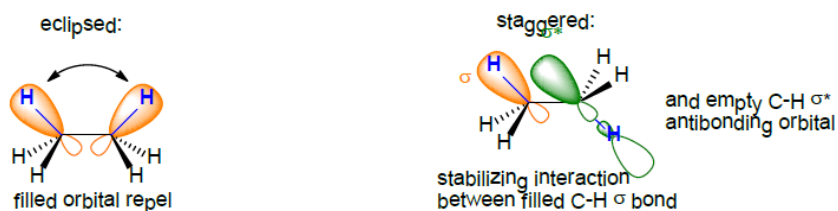
The rotational barrier in this case is said to be 12 kJ mol<sup>-1</sup>. This is the energy required to convert the stable staggered form to the unstable eclipsed form (Figure 5). The change in energy on going from staggered form to eclipsed form and vice versa is plotted in with respect to the dihedral angle. The angle between two intersecting planes on a third plane normal to the

intersection of the two planes is called dihedral angle. In this case the dihedral angle is angle between the planes containing the atoms 1 and 2 and the plane containing the atoms 3 and 4.



**Figure 2**

The conformational analysis of ethane is given below. Thus, between these two extremes, there are lots of other conformations and energy change is gradual in nature. However, this does not mean that the ethane spends equal time in all conformations. In fact it mostly stays at the bottom of the potential well (staggered conformation). Obviously, it comes to mind whether the hydrogen atoms are bulky enough to cause a change in the energy states of the eclipsed and staggered conformation. As a matter of fact, this occurs due to the fact that the electrons in the bonds repel each other and this repulsion is at a maximum in the eclipsed conformation. There may be some stabilizing interaction between the C-H  $\sigma$ -bonding orbital on one carbon and the C-H  $\sigma^*$  anti-bonding orbital on the other carbon, which is greatest when the two orbitals are exactly parallel: this only happens in the staggered conformation (Figure 3).

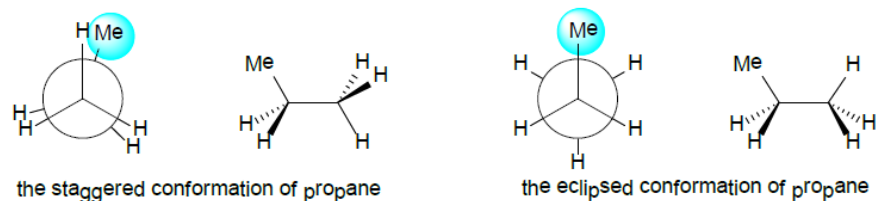


**Figure 3**



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As the hydrocarbon chain size increases, more complex effects seem to effect the energy considerations of the conformations (Figure 4). In the conformational study of propane, the conformational analysis can be done either along the C1-C2 bond or the C2-C3 bond-both being identical. In this case, the rotational barrier being  $14 \text{ kJmol}^{-1}$  is only slightly more than that of ethane. Thus the conformational analysis diagram is almost similar to ethane.



**Figure 4**

With butane, there are two methyl groups if we consider the C2-C3 bond as the pivotal bond for rotation. Here, the two methyl groups could eclipse each other in a conformation and since the steric hindrance due to this should be significant enough, so the potential energy will be highest for this conformation. The other eclipsed conformations will have a methyl group eclipsed by hydrogen which will be lower in energy than the former. Similarly, for the staggered conformations, there will be two types of staggered conformations differing in energy. Hence the terms eclipsed and staggered are insufficient to describe the conformations.

A new system of naming the conformational isomers is thus devised (Figure 5). The term torsion angle is defined as the angle (having an absolute value between  $0^\circ$  and  $180^\circ$ ) between bonds to two specified groups, one from the atom nearer (proximal) to the observer and the other from the further (distal) atom in a Newman projection. The torsion angle between groups A and D is then considered to be positive if the bond A-B is rotated in a clockwise direction through less than  $180^\circ$  in order that it may eclipse the bond C-D: a negative torsion angle requires rotation in the opposite sense. Stereochemical arrangements corresponding to torsion angles between  $0^\circ$  and  $\pm 90^\circ$  are called syn (s), those corresponding to torsion angles between  $\pm 90^\circ$  and  $180^\circ$  anti (a). Similarly, the arrangements corresponding to torsion angles between  $30^\circ$  and  $150^\circ$  or between  $-30^\circ$  and  $-150^\circ$  are called clinal (c) and those between  $0^\circ$  and  $30^\circ$  or  $150^\circ$  and  $180^\circ$  are called periplanar (p). The two types of terms can be combined so as to define four ranges of torsion



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angle;  $0^\circ$  to  $30^\circ$  synperiplanar (sp);  $30^\circ$  to  $90^\circ$  and  $-30^\circ$  to  $-90^\circ$  synclinal (sc);  $90^\circ$  to  $150^\circ$ , and  $-90^\circ$  to  $-150^\circ$  anticlinal (ac);  $\pm 150^\circ$  to  $180^\circ$  antiperiplanar (ap). The synperiplanar conformation is also known as the syn- or cis-conformation; antiperiplanar as anti or trans and synclinal as gauche or skew.

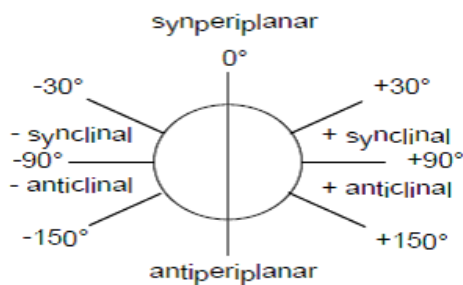


Figure 5

According to this system, the conformational isomers of butane due to rotation about the C2-C3 bond may be named as:

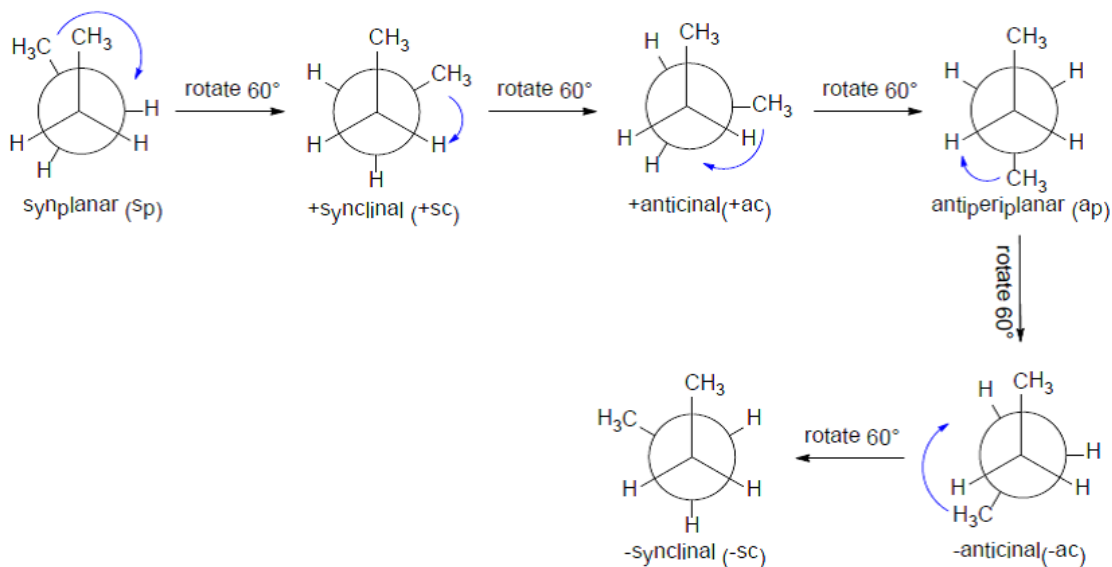


Figure 6

Thus, the conformational analysis diagram of the different conformational isomers of n-butane due to rotation about C2-C3 bond as a function of dihedral angle is given below (Figure 7). As expected the synperiplanar conformer having methyl groups eclipsed with each other has the



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highest energy and is least stable. The other eclipsed conformations have lower energy than the synperiplanar conformer. These are the two anticlinal conformations. The staggered conformers also show a similar pattern. Thus, there are two synclinal conformers (also called gauche conformers) where the two methyl groups are at an angle of  $60^\circ$  to each other. If we consider angle of torsion then the two anticlinal conformers may be differentiated according to the sense of rotation of the angle of torsion. Thus they may be termed as +anticlinal (P-gauche) for a positive angle of torsion or -anticlinal (M-gauche) for a negative angle of torsion. The anticlinal conformations may also be prefixed with + or - to denote the angle of torsion.

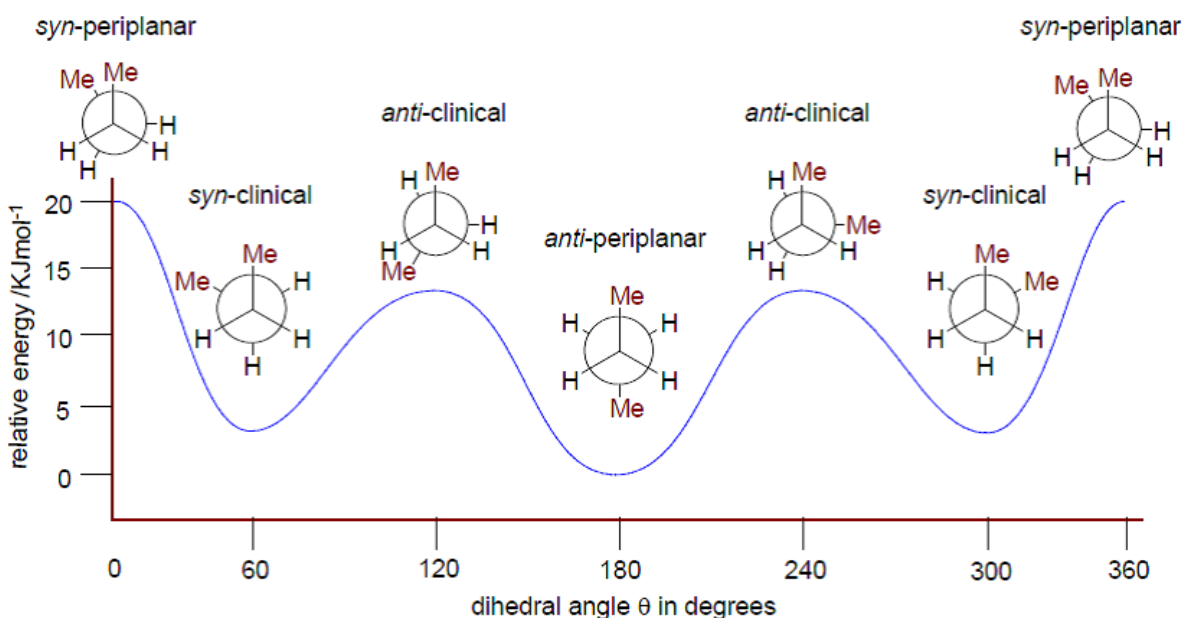


Figure 7

The compounds considered so far are linear compounds and thus rotation about carbon-carbon bond is easily possible. However, it is expected that this rotation will be hindered in cyclic compounds. Also, the hindrance will be large in small rings compared to large rings. This brings to a new concept- Bayer's ring strain.

In alicyclic compounds, all the carbons are  $sp^3$  hybridized and thus the bond angle should be  $109^\circ$  ideally. But in a small planar ring, like that of cyclopropane it is not possible to achieve this bond angle. As such the actual bond angle in cyclopropane is  $60^\circ$  instead of  $109^\circ$ . This thus introduces a strain in the molecule known as ring strain. According to Bayer, this strain would



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increase as rings grow larger and smaller than cyclopentane, they should show increasing angular strain and increasing strain energy.

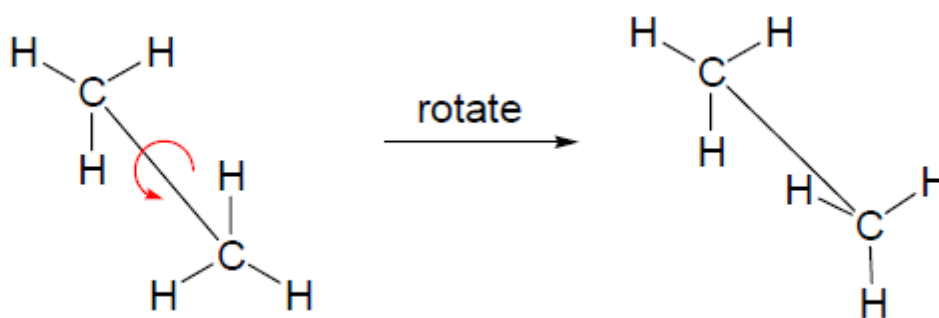
In reality, a different scenario emerges as it is observed that, the cyclopropane ring is highly strained, the ring strain decreases with ring size and reaches a minimum for cyclohexane and not cyclopropane. The ring strain then increases but not as rapidly as is expected by Bayer's theory and reaches a maximum at cyclononane and then decreases again. As the number of ring carbons increase beyond 14, the ring strain remains roughly constant.

## EXAMPLE:

### 4.1 Conformation of Ethane

**conformation:** the different arrangements of atoms that result from rotation about a single bond

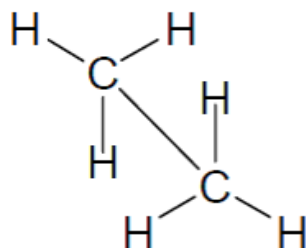
**conformers:** a specific conformation (conformational isomer); same connections of atoms



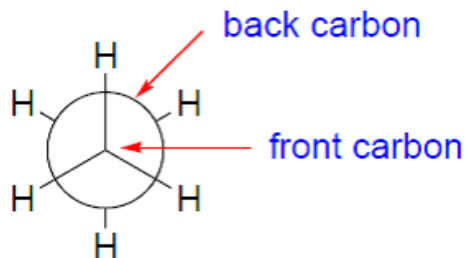


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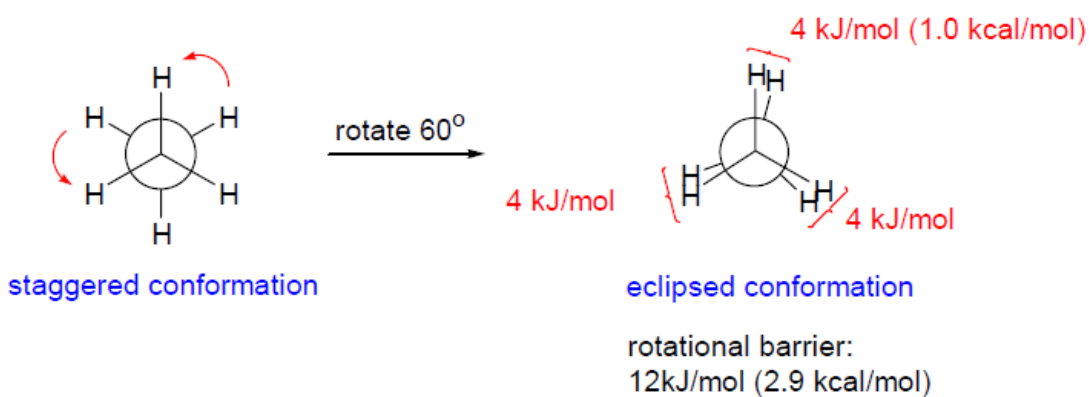
### Sawhorse representation



### Newman projection

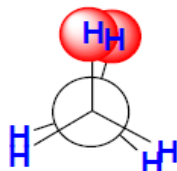


**Energy barrier for rotation:** not perfectly free rotation about  $\sigma$ -bonds



- the 12 kJ/mol (2.9 kcal/mol) of extra energy present in the eclipsed conformation of ethane is called **torsional strain**

• **Torsional strain** is due to repulsion between electron clouds in the C-H bonds as they pass close by each other in the eclipsed conformer

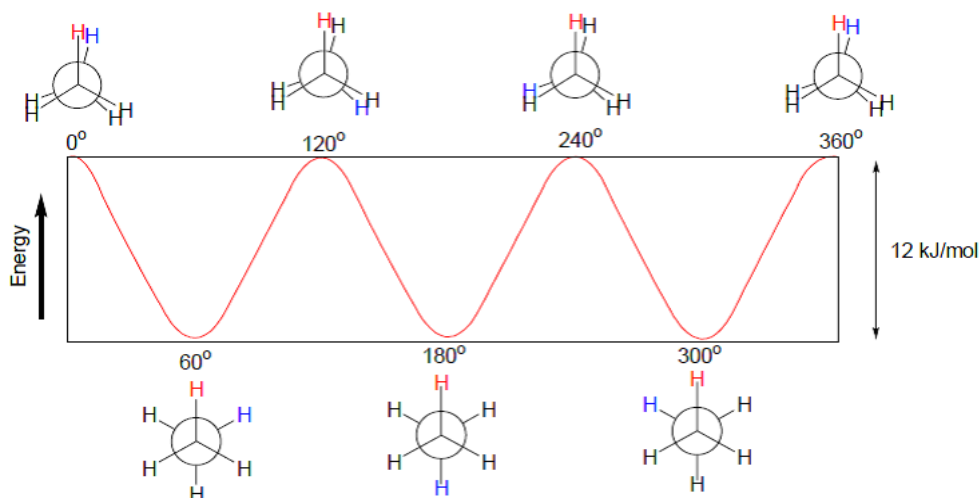


eclipsed conformation

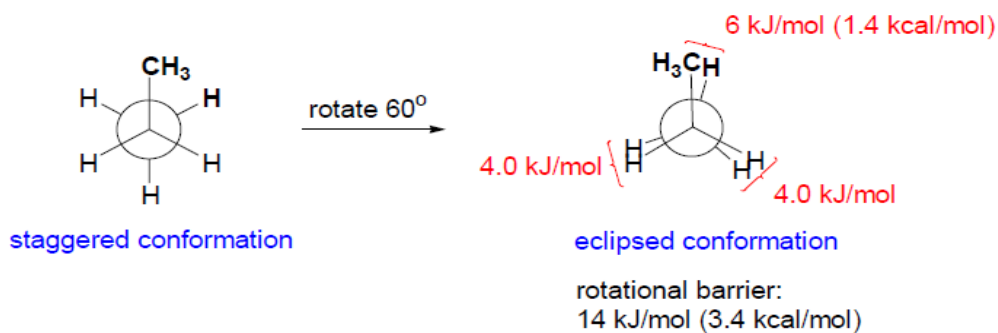


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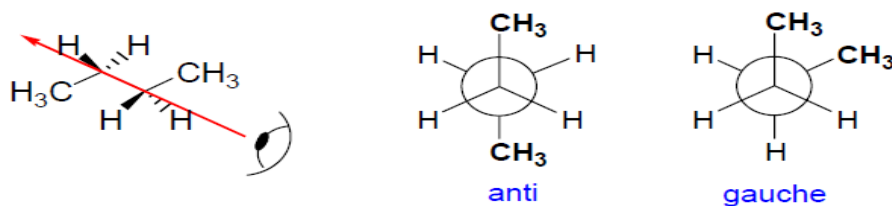
A graph of potential energy versus bond rotation in ethane



### 4.2 Conformation of Propane



### 4.3 Conformation of Butane



anti conformation: two large groups are in the opposite side

eclipsed conformations

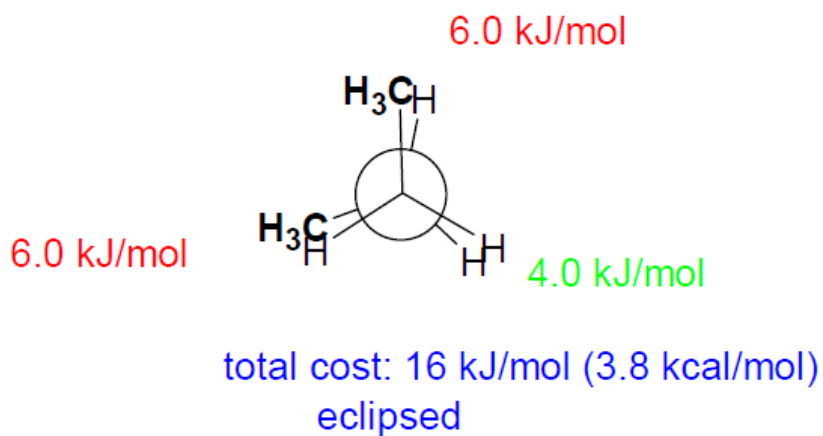
gauche conformation: two large groups are 60° apart



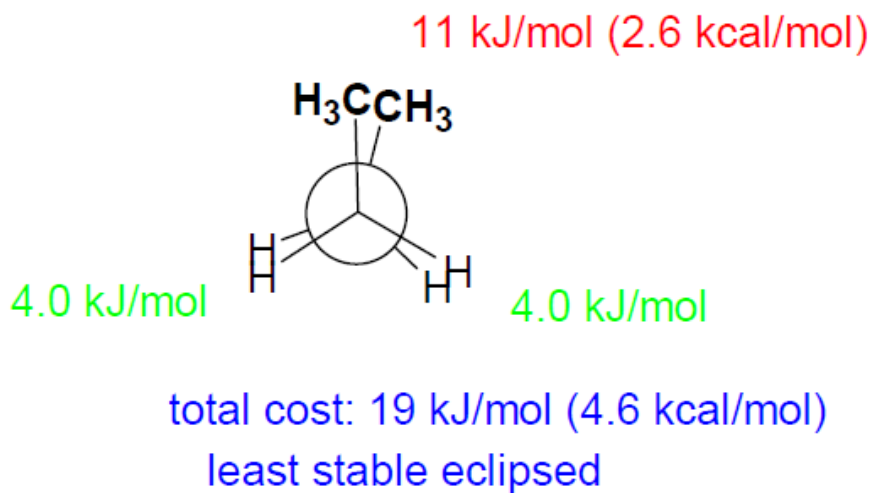


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Eclipsed conformations



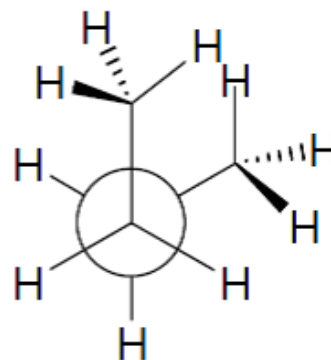
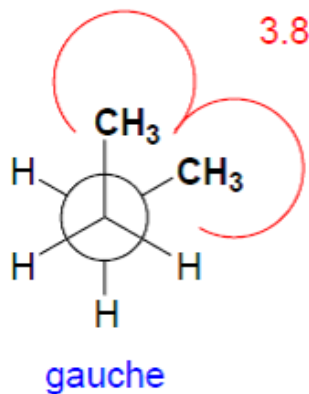
Eclipsed conformations





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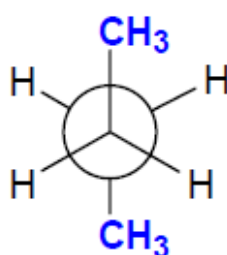
**Gauche conformation:** 3.8 kJ/mol (0.9 kcal/mol) unstable due to steric strain between two methyl groups



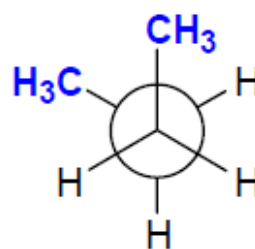
- hydrogen atoms on methyl groups interact

steric strain: repulsive interaction that occurs when atoms are too closer

Four possible  
conformations of  
*n*-butane

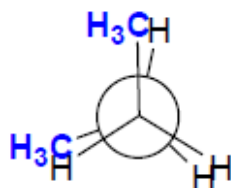


anti

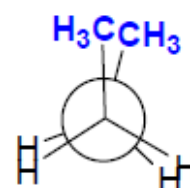


gauche

staggered

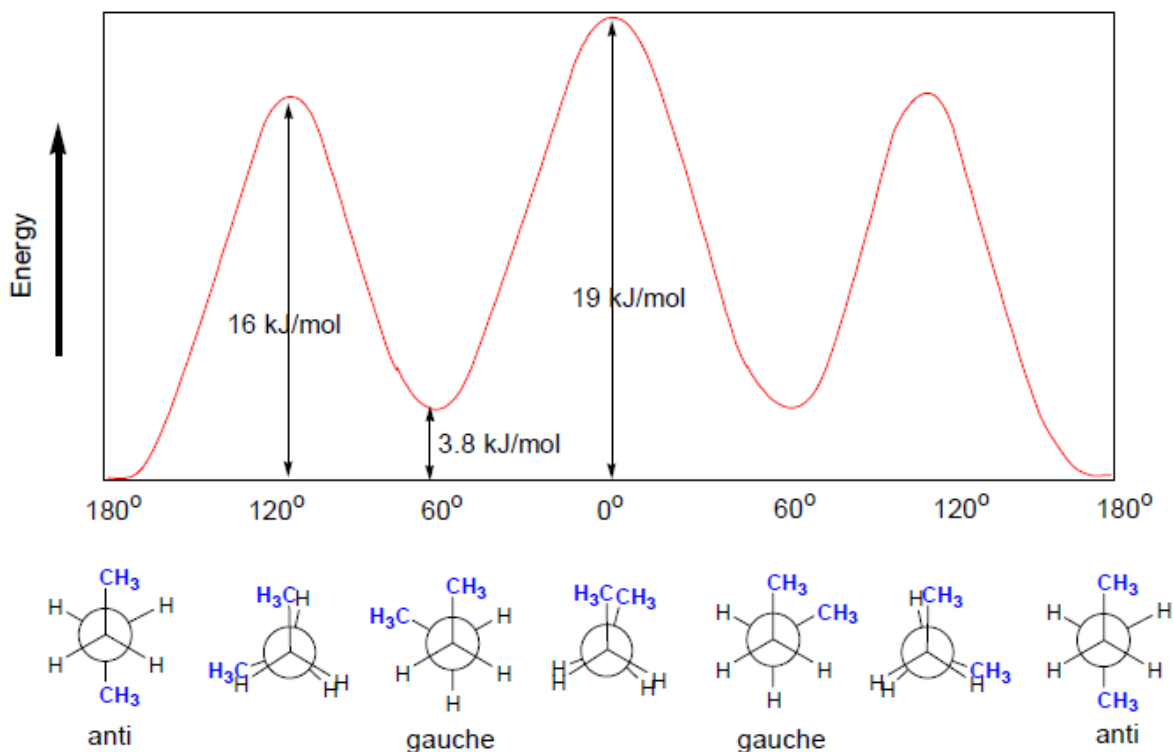


eclipsed

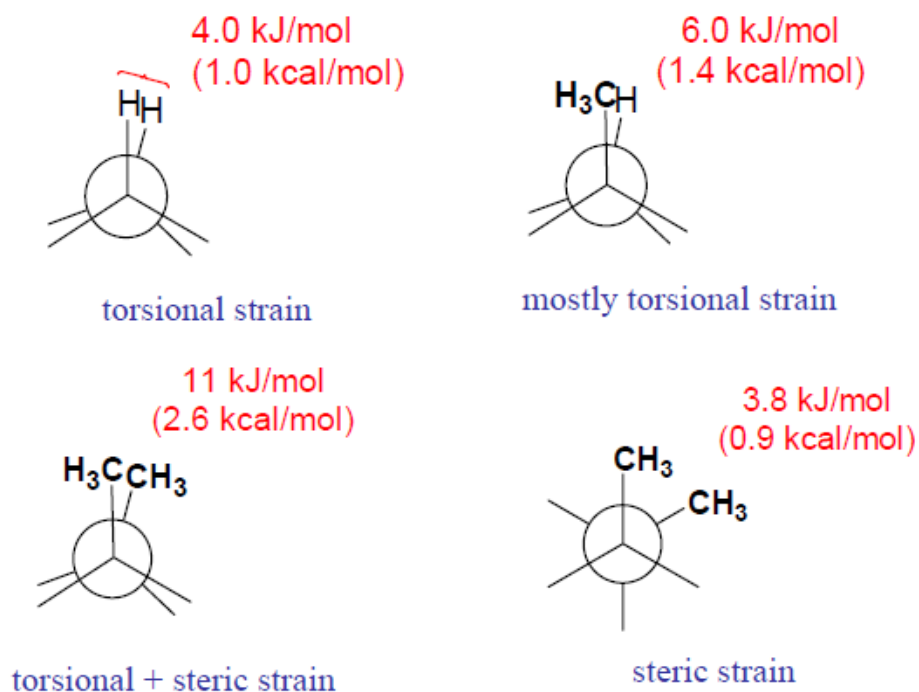


eclipsed

A graph of potential energy versus bond rotation in butane



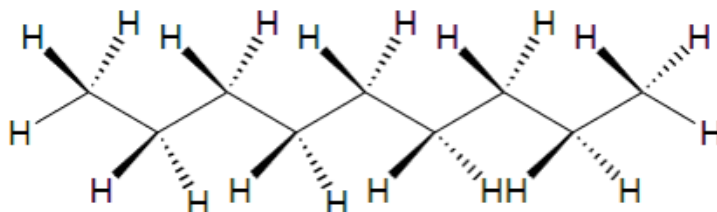
Energy costs for interactions in alkane conformers





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- the most stable conformation of any alkanes has the C-C bonds in staggered arrangements and large substituents arranged *anti* to each other



zig-zag conformation

- At room temperature, enough thermal energy is present to cause rotation around  $\sigma$ -bonds to occur rapidly so that all conformations are in equilibrium. At any given time, however, a larger percentage of molecules will be found in a more stable conformation than in a less stable one.

Source: NPTEL