Conformational isomers are essentially different shapes of the same molecule resulting from rotation round C–C single bonds. Conformational isomers are not different compounds and are freely interconvertable. Unlike constitutional and configurational isomers, conformational isomers cannot be separated.

### Alkanes

Alkanes can take up different shapes or conformations due to rotation around the C–C bonds. The most stable conformations are those where the bonds are staggered, rather than eclipsed. The torsional angle in butane is the angle between the first and third C–C bonds when viewed along the middle C–C bond. The most stable conformation of butane has a torsional angle of 180° where the carbon atoms and the C–C bonds are as far apart from each other as possible. The other possible staggered conformation has a torsional angle of 60° which results in some steric and electronic strain – called a gauche interaction. The most stable conformation for a straight chain alkane is zigzag shaped where all the torsional angles are at 180°.

Cycloalkanes can adopt different conformations or shapes. The most stable conformation for cyclohexane is the chair. Each carbon in the chair has two C–H bonds, one of which is equatorial and one of which is axial. A chair structure can invert through a high energy boat intermediate such that the equatorial bonds become axial and the axial bonds become equatorial. If a substituent is present, the most stable chair conformation is where the substituent is equatorial. In the axial position, the substituent experiences two gauche interactions with C–C bonds in the ring.
sphere. Viewed in this way, it can be seen that the C–H bonds on carbon 1 are eclipsed with the C–H bonds on carbon 2 in conformation II.

Of these two conformations, the staggered conformation is the more stable since the C–H bonds and hydrogen atoms are as far apart from each other as possible. In the eclipsed conformation, both the bonds and the atoms are closer together and this can cause strain due to electron repulsion between the eclipsed bonds and between the eclipsed atoms. Therefore, the vast majority of ethane molecules are in the staggered conformation at any one time. However, it is important to realize that the energy difference between the staggered and eclipsed conformations is still small enough to allow each ethane molecule to pass through an eclipsed conformation (Fig. 3) – otherwise C–C bond rotation would not occur.

Ethane has only one type of staggered conformation, but different staggered conformations are possible with larger molecules such as butane (Fig. 4). The first
and the third C–C bonds in isomer I are at an angle of 60° with respect to each other when viewed along the middle C–C bond. In isomer II, these bonds are at an angle of 180°. This angle is known as the torsional angle or dihedral angle. Isomer II is more stable than isomer I. This is because the methyl groups and the C–C bonds in this conformer are as far apart from each other as possible. The methyl groups are bulky and in conformation I they are close enough to interact with each other and lead to some strain. There is also an interaction between the C–C bonds in isomer I since a torsional angle of 60° is small enough for some electronic repulsion to exist between the C–C bonds. When C–C bonds have a torsional angle of 60°, the steric and electronic repulsions which arise are referred to as a gauche interaction.

As a result, the most stable conformation for butane is where the C–C bonds are at torsional angles of 180° which results in a ‘zigzag’ shape. In this conformation, the carbon atoms and C–C bonds are as far apart from each other as possible. The most stable conformations for longer chain hydrocarbons will also be zigzag (Fig. 5). However, since bond rotation is occurring all the time for all the C–C bonds, it is unlikely that many molecules will be in a perfect zigzag shape at any one time.

**Cycloalkanes**

Cyclopropane (Fig. 6) is a flat molecule as far as the carbon atoms are concerned, with the hydrogen atoms situated above and below the plane of the ring. There are no conformational isomers. Cyclobutane (Fig. 7) on the other hand can form three distinct shapes – a planar shape and two ‘butterfly’ shapes. Cyclopentane (Fig. 8) can also form a variety of shapes or conformations. The planar structures for cyclobutane and cyclopentane are too strained to exist in practice due to eclipsed C–H bonds.

The two main conformational shapes for cyclohexane are known as the chair and the boat (Fig. 9). The chair is more stable than the boat since the latter has eclipsed C–C and C–H bonds. This can be seen better in the Newman projections (Fig. 10) which have been drawn such that we are looking along two bonds at the same time – bonds 2–3 and 6–5. In the chair conformation, there are no eclipsed
C–C bonds. However, in the boat conformation, bond 1–2 is eclipsed with bond 3–4, and bond 1–6 is eclipsed with bond 5–4. This means that the boat conformation is less stable than the chair conformation and the vast majority of cyclohexane molecules exist in the chair conformation. However, the energy barrier is small enough for the cyclohexane molecules to pass through the boat conformation in a process called ‘ring flipping’ (Fig. 11). The ability of a cyclohexane molecule to ring-flip is important when substituents are present. Each carbon atom in the chair structure has two C–H bonds, but these are not identical (Fig. 12). One of these bonds is termed **equatorial** since it is roughly in the plane of the ring. The other C–H bond is vertical to the plane of the ring and is called the **axial** bond.

When ring flipping takes place from one chair to another, all the axial bonds become equatorial bonds and all the equatorial bonds become axial bonds. This does not matter for cyclohexane itself, but it becomes important when there is a
substituent present in the ring. For example, methylcyclohexane can have two chair structures where the methyl group is either on an equatorial bond or on an axial bond (Fig. 13).

These are different shapes of the same molecule which are interconvertible due to rotation of C–C single bonds (the ring flipping process). The two chair structures are conformational isomers but they are not of equal stability. The more stable conformation is the one where the methyl group is in the equatorial position. In this position, the C–C bond connecting the methyl group to the ring has a torsional angle of 180° with respect to bonds 5–6 and 3–2 in the ring. In the axial position, however, the C–C bond has a torsional angle of 60° with respect to

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\text{Torsion angle} = 180^\circ
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\text{Torsion angle} = 60^\circ
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Fig. 12. (a) Equatorial C–H bonds; (b) axial C–H bonds.

Fig. 13. Ring flipping of methylcyclohexane.

Fig. 14. Newman projections of the chair conformations of methylcyclohexane.
these same two bonds. This can be illustrated by comparing Newman diagrams of
the two methylcyclohexane conformations (Fig. 14).

A torsion angle of $60^\circ$ between C–C bonds represents a gauche interaction and
so an axial methyl substituent experiences two gauche interactions with the cyclo-
hexane ring whereas the equatorial methyl substituent experiences none. As a
result, the latter chair conformation is preferred and about 95% of methylcyclo-
hexane molecules are in this conformation at any one time, compared to 5% in the
other conformation.