In Section 1.3B, we learned that understanding the structures of many molecules requires that we specify not only their bond lengths and bond angles but also their dihedral angles. In this section, we’ll use the simple alkanes ethane and butane to develop some widely applicable simple principles that will allow us to predict the dihedral angles in more complex molecules.

### A. Conformation of Ethane

To specify the dihedral angles in ethane, we must define the relationship between the C—H bonds on one carbon and those on the other. A convenient way to do this is to view the molecule in a Newman projection. A **Newman projection** is a type of planar projection along one bond, which we’ll call the *projected bond*. For example, suppose we wish to view the ethane molecule in a Newman projection along the carbon–carbon bond, as shown in Fig. 2.2. In this projection, the carbon–carbon bond is the projected bond. To draw a Newman projection, start with a circle. The remaining bonds to the *nearer* atom in the projected bond are drawn to the center of the circle. The remaining bonds to the *farther* atom in the projected bond are drawn to the periphery of the circle. In the Newman projection of ethane (Fig. 2.2c), the three C—H bonds on one carbon are hidden.

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(a) viewing a model of ethane from one end 
(b) end-on view 
(c) Newman projection

*Figure 2.2* How to derive a Newman projection for ethane using ball-and-stick models (top) and line-and-wedge formulas (bottom). (The hydrogens and C—H bonds farthest from the observer are shown in blue.) First view the ethane molecule from the end of the bond you wish to project, as in part (a). The resulting end-on view is shown in part (b). This is represented as a Newman projection (c) in the plane of the page. In the Newman projection, the bonds drawn to the center of the circle are attached to the carbon closer to the observer; the bonds drawn to the periphery of the circle (blue) are attached to the carbon farther from the observer. The projected bond (the carbon–carbon bond) is hidden.
bonds drawn to the center of the circle are bonds to the front carbon. The C—H bonds to the periphery of the circle are the bonds to the rear carbon. The projected bond itself, which is the fourth bond to each carbon, is hidden.

The Newman projection of ethane makes it very easy to see the dihedral angles \( \theta \) between its C—H bonds. When we have specified all of the dihedral angles in a molecule, we have specified its conformation. Thus, the conformation of a molecule is the spatial arrangement of its atoms when all of its dihedral angles are specified. We can also refer to conformations of parts of molecules, for example, conformations about individual bonds.

Two limiting possibilities for the conformation of ethane can be seen from its Newman projections; these are termed the staggered conformation and the eclipsed conformation.

In the staggered conformation, a C—H bond of one carbon bisects the angle between two C—H bonds of the other. The smallest dihedral angle in the staggered conformation is \( \theta = 60^\circ \). (The other dihedral angles are \( \theta = 180^\circ \) and \( \theta = 300^\circ \).) In the eclipsed conformation, the C—H bonds on the respective carbons are superimposed in the Newman projection. The smallest dihedral angle is \( \theta = 0^\circ \). (The other dihedral angles are \( \theta = 120^\circ \) and \( \theta = 240^\circ \).) Of course, conformations intermediate between the staggered and eclipsed conformations are possible, but these two conformations will prove to be of central importance.

Which is the preferred conformation of ethane? The energies of the ethane conformations can be described by a plot of relative energy versus dihedral angle, which is shown in Fig. 2.3 on p. 52. In this figure, the dihedral angle is the angle between the bonds to the colored hydrogens on the different carbons. To see the relationships in Fig. 2.3, build a model of ethane, hold either carbon fixed, and turn the other carbon about the C—C bond. As the angle of rotation changes, the model passes alternately through three identical staggered and three identical eclipsed conformations. As shown by Fig. 2.3, identical conformations have identical energies. The graph also shows that the eclipsed conformation is characterized by an energy maximum, and the staggered conformation is characterized by an energy minimum. The staggered conformation is therefore the more stable conformation of ethane. The graph shows that the staggered conformation is more stable than the eclipsed conformation by about 12 kJ mol\(^{-1}\) (about 2.9 kcal mol\(^{-1}\)). This means that it would take about 12 kJ of energy to convert one mole of staggered ethane into one mole of eclipsed ethane.

The reason for the relative stability of the staggered conformation has been debated for years. One theory is that the staggered form is more stable because there is a favorable interaction between the bonding and antibonding molecular orbitals associated with the C—H bonds on the two carbons that lie at a dihedral angle of 180°. This dihedral angle, and hence the stabilizing interaction, is only possible in the staggered form. A second theory holds that there is repulsion between the electrons in the C—H bonds on the two carbons. Because the bonds are closer when they have a dihedral angle of 0°, this repulsion is greater in the eclipsed form. This repulsion is termed torsional strain. Notice that the repulsion is not between the hydrogens but between the electrons in the bonds themselves. An assessment in 2007 of the two effects indicated that torsional strain accounts for about 75% of the energy difference.
between the eclipsed and staggered forms, and that the favorable orbital interaction accounts for about 25%.

One staggered conformation of ethane can convert into another by rotation of either carbon relative to the other about the carbon–carbon bond. Such a rotation about a bond is called an internal rotation (to differentiate it from a rotation of the entire molecule). When an internal rotation occurs, an ethane molecule must briefly pass through the eclipsed conformation. To do so, it must acquire the additional energy of the eclipsed conformation and then lose it again. What is the source of this energy?

At temperatures above absolute zero, molecules are in constant motion and therefore have kinetic energy. Heat is a manifestation of this kinetic energy. In a sample of ethane, the molecules move about in a random manner, much as people might mill about in a large crowd. These moving molecules frequently collide, and molecules can gain or lose energy in such collisions. (An analogy is the collision of a bat with a ball; some of the kinetic energy of the bat is lost to the ball.) When an ethane molecule gains sufficient energy from a collision, it can undergo internal rotation, passing through the more energetic eclipsed conformation into another staggered conformation. Whether a given ethane molecule acquires sufficient energy to undergo an internal rotation is strictly a matter of probability (random chance). However, an internal rotation is more probable at higher temperature because warmer molecules have greater kinetic energy.

The probability that ethane undergoes internal rotation is reflected as its rate of rotation: how many times per second the molecule converts from one staggered conformation into another. This rate is determined by how much energy must be acquired for the rotation to occur: the more energy required, the smaller the rate. In the case of ethane, 12 kJ mol⁻¹ (2.9 kcal mol⁻¹) is required. This amount of energy is small enough that the internal rotation of ethane

![Figure 2.3 Variation of energy with dihedral angle about the carbon–carbon bond of ethane. In this diagram, the rear carbon is held fixed and the front carbon is rotated, as shown by the green arrows. The dihedral angle plotted is the angle between the bonds to the red and blue hydrogens. Note that the staggered conformations are at the energy minima, and the eclipsed conformations are at the energy maxima.](image-url)
is very rapid even at very low temperatures. At 25 °C, a typical ethane molecule undergoes a rotation from one staggered conformation to another at a rate of about $10^{11}$ times per second! This means that the interconversion between staggered conformations takes place about once every $10^{-11}$ second. Despite this short lifetime for any one staggered conformation, an ethane molecule spends most of its time in its staggered conformations, passing only transiently through its eclipsed conformations. Thus, an internal rotation is best characterized not as a continuous spinning but as a constant succession of jumps from one staggered conformation to another.

### B. Conformations of Butane

Butane contains two distinguishable types of carbon–carbon bonds: the two terminal C—C bonds (blue), and the central C—C bond (red).

\[
\begin{align*}
H_3C-CH_2-CH_2-CH_3 \\
\text{butane}
\end{align*}
\]

We’ll consider internal rotation about the central C—C bond. This rotation is a bit more complex than the ethane case, but examination of this rotation leads to important new insights about molecular conformation. As with ethane, we use Newman projections, as shown in Fig. 2.4. Remember again that the projected bond—the central C—C bond in this case—is hidden in the Newman projection.

---

**Figure 2.4** How to derive the Newman projection of the central carbon–carbon bond in butane using ball-and-stick models (top) and line-and-wedge formulas (bottom). The bonds and groups on the rear carbon of the projected bond are shown in blue. (Only one of the butane conformations is shown.)
The graph of energy as a function of dihedral angle in butane is given in Fig. 2.5. Note once again that the various rotational possibilities are generated with a model by holding either carbon fixed (the carbon away from the observer in Fig. 2.5) and rotating the other one.

Figure 2.5 shows that the staggered conformations of butane, like those of ethane, are at energy minima and are thus the stable conformations of butane. However, not all of the staggered conformations (nor all of the eclipsed conformations) of butane are alike. The different staggered conformations have been given special names. The conformations with a dihedral angle of 60° and 300° in Fig. 2.5 (or ±60°) between the two CH₃ bonds are called gauche conformations (from the French gauche, meaning “to turn aside”); the form in which the dihedral angle is 180° is called the anti conformation.

The relationship between bonds also can be described with the terms gauche and anti. Two bonds that have a dihedral relationship of ±60° are said to be gauche bonds. Two bonds that
have a dihedral relationship of 180° are said to be **anti bonds**. Notice that these terms refer to bonds on adjacent carbons.

Figure 2.5 shows that the gauche and anti conformations of butane have different energies. The anti conformation is the more stable of the two by 2.80 kJ mol\(^{-1}\) (0.67 kcal mol\(^{-1}\)). The gauche conformation is the less stable of the two because the CH\(_3\) groups are very close together—so close that the hydrogens on the two groups occupy each other’s space. You can see this with the aid of the space-filling model in Fig. 2.6a.

This problem can be discussed more precisely in terms of atomic size. One measure of an atom’s effective size is its **van der Waals radius**. Energy is required to force two nonbonded atoms together more closely than the sum of their van der Waals radii. Because the van der Waals radius of a hydrogen atom is about 1.2 Å, forcing the centers of two nonbonded hydrogens to be closer than twice this distance requires energy. Furthermore, the more the two hydrogens are pushed together, the more energy is required. The extra energy required to force two nonbonded atoms within the sum of their van der Waals radii is called a **van der Waals repulsion**. Thus, to attain the gauche conformation, butane must acquire more energy. In other words, gauche-butane is destabilized by van der Waals repulsions between nonbonded hydrogens on the two CH\(_3\) groups. Such van der Waals repulsions are absent in anti-butane (see Fig. 2.6b). Thus, anti-butane is more stable than gauche-butane.

As with ethane, the eclipsed conformations of butane are destabilized by torsional strain. But, in the conformation in which the two C—CH\(_3\) bonds are eclipsed, the major source of instability is van der Waals repulsions between the methyl hydrogens (Fig. 2.6c), which are forced to be even closer than they are in the gauche conformation. Notice that this is the most unstable of the eclipsed conformations (θ = 0° in Fig. 2.5).

It is important to understand the relative energies of the butane conformations because, when different stable conformations are in equilibrium, the most stable conformation—the conformation of lowest energy—is present in greatest amount. Thus, the anti conformation of butane is the predominant conformation of butane. At room temperature, there are about twice as many molecules of butane in the anti conformation as there are in the gauche conformation.

---

**Figure 2.6** Space-filling models of different butane conformations with the methyl hydrogens shown in color. (a) Gauche-butane. A hydrogen atom from one CH\(_3\) group is so close to a hydrogen atom of the other CH\(_3\) group that these hydrogens, shown in pink, violate each other’s van der Waals radii. The resulting van der Waals repulsions cause gauche-butane to have a higher energy than anti-butane, in which this interaction is absent. (b) Anti-butane. This conformation is most stable because it contains no van der Waals repulsions. (c) Butane with the C—CH\(_3\) bonds eclipsed. In this conformation, van der Waals repulsions between the hydrogens of the two CH\(_3\) groups (pink) are even greater than they are in gauche-butane.
The gauche and anti conformations of butane interconvert rapidly at room temperature—almost as rapidly as the staggered forms of ethane. Because the eclipsed conformations lie at energy maxima and are unstable, they do not exist to any measurable extent.

The investigation of molecular conformations and their relative energies is called conformational analysis. In this section, we’ve learned some important principles of conformational analysis that we’ll be able to apply to more complex molecules. Here is a summary of these principles:

1. Staggered conformations about single bonds are favored.
2. Van der Waals repulsions (repulsions between nonbonded atoms) occur when atoms are “squeezed” closer together than the sum of their van der Waals radii.
3. Conformations containing van der Waals repulsions are less stable than conformations in which such repulsions are absent.
4. Rotation about C—C single bonds is so rapid that it is hard to imagine separating conformations except at very low temperature.

**Study Problem 2.1**

Draw a Newman projection for the anti conformation about the C3–C4 bond of 2-methylhexane, viewing the bond so that C3 is nearest the observer.

**Solution** First draw a “blank” Newman projection to represent the projected bond. Remember that the projected bond itself (the C3–C4 bond) is invisible in the projection. Either template below can be used.

We arbitrarily pick the template on the left. In the view dictated by the problem, the front carbon is C3. Identify the three groups attached to C3 with bonds other than the projected bond. These groups are H, H, and the H3C—CH— group. Put these on the front carbon of the Newman projection. *It doesn’t matter which bonds go to which groups as long as all groups are on the front carbon.* It’s important to understand that, because we are not examining the bonds within the large group, we can condense this group to (CH3)2CH—or even C3H7—.

We then identify the groups attached to the back carbon (C4) by bonds other than the projected bond. These groups are H, H, and —CH2CH3. Now it does matter where we put these groups, because we are asked for the anti conformation. The —CH3CH3 group must be placed anti to the (CH3)2CH— group. Remember that “anti” means a dihedral angle of 180°.
2.3 (a) Draw a Newman projection for each conformation about the C2—C3 bond of isopentane, a compound containing a branched carbon chain.

\[
\begin{align*}
H_3C & \quad CH \quad CH_2 \quad CH_3 \\
& \quad CH_3
\end{align*}
\]

isopentane

Show both staggered and eclipsed conformations.

(b) Sketch a curve of potential energy versus dihedral angle for isopentane, similar to that of butane in Fig. 2.5. Label each energy maximum and minimum with one of the conformations you drew in part (a).

(c) Which conformations are likely to be present in greatest amount in a sample of isopentane? Explain.

2.4 Repeat the analysis in Problem 2.3 for either one of the terminal bonds of butane.

2.4 CONSTITUTIONAL ISOMERS AND NOMENCLATURE

A. Isomers

When a carbon atom in an alkane is bound to more than two other carbon atoms, a branch in the carbon chain occurs at that position. The smallest branched alkane has four carbon atoms. As a result, there are two four-carbon alkanes; one is butane, and the other is isobutane.

\[
\begin{align*}
H_3C & \quad CH \quad CH_2 \quad CH_3 \\
& \quad CH \quad CH_3
\end{align*}
\]

butane \[\text{bp } -0.5^\circ\]

\[
\begin{align*}
H_3C & \quad CH \quad CH_2 \quad CH_3 \\
& \quad CH \quad CH_3
\end{align*}
\]

isobutane \[\text{bp } -11.7^\circ\]

These are different compounds with different properties. For example, the boiling point of butane is \(-0.5^\circ\) C, whereas that of isobutane is \(-11.7^\circ\) C. Yet both have the same molecular for-