2 Ethane

Aims

In this chapter you will learn about the rotation about the carbon-carbon single bond of ethane and the effect of rotation on the shape and energy of the ethane molecule. The study of the relation between the rotation of single bonds and the molecular structure and that with the molecular energy is called conformational analysis.

With the aid of the Newman projection formula, the conformational analyses of propane, butane and polysubstituted ethanes will be presented. Naming the conformers will also be presented by expanding the sequence rule.

New terms and concepts

- flying-wedge representation
- perspective representation
- Newman projection
- conformational analysis
- dihedral angle-energy diagram
- conformer
- twist angle
- twist angle-energy diagram
- eclipsed
- skew
- anti
- gauche
- periplanar
- clinal

Goals of this chapter

After you master this chapter successfully, you will be able to do the following:
1. To draw the Newman projection of ethane in any conformation.
2. To draw a dihedral angle-energy diagram in describing the energy change of ethane by the rotation about a single bond.
3. To distinguish eclipsed and staggered conformations.
4. To distinguish two staggered conformers, anti form and gauche form, in the conformational analysis of butane.
5. To understand the nomenclature of conformers based on the sequence rule.

2.1 The Newman Projection

The rotation about the C-C single bond of ethane and related molecules to induce a change of molecular shape is well understood. It is necessary, however, to establish a set of rules beforehand in order to express the change of three-dimensional structures with two-dimensional drawings.

Schematic Drawings

The first step in expressing molecular structures in a two-dimensional way is the use of schematic drawings; i.e., drawing molecular structures as they appear to be. In order to stress the three-dimensional nature, several conventions have been devised. Perspective and flying wedge drawings are typical examples.
It is impossible, however, for these drawings to represent the exact shape of molecules. As we have learned before, the dihedral angle formed by four atoms, H-C-C-H, is a very good parameter of molecular structure. It is not practical, however, to draw such a figure as Fig. 1.8 for large compounds.

In order to solve that problem, a method of drawing molecular structure was proposed by the American chemist M. S. Newman in the middle of the 20th century. The essential characteristic of this method is that the dihedral angle is clearly demonstrated. The way of drawing a Newman projection is exemplified by that of ethane. The molecule (or rather, molecular model) of ethane is projected against the wall behind the molecule along the direction of the C-C bond. On the wall, the shadows of six hydrogens and two carbons should appear.

However, since the projection is made along the C-C bond, the two carbon atoms overlapped and only the carbon in front can be seen as the other one is behind it. To avoid this inconvenience, the front carbon is now designated as a dot, while a large circle portrays the back carbon. The dihedral angle is defined by the angle made by the two bonds, $C_A-H_A$ and $C_B-H_B$ on the Newman projection. In Fig. 2.2(a), the Newman projection is shown, and in Fig. 2.2(b), the two conformations of ethane, 1 and 2, are shown.

Indeed, the Newman projection is a shadowgraph!
2.2 Conformational analysis of ethane

Then how can we describe the relation between 1 and 2? They are stereoisomers of each other since the spatial relation among the eight atoms constituting each ethane differ. The difference is, however, not the same as the one observed for 14 and 15 of Ch. 1 (the two enantiomers of CHFCIBr). Compounds 14 and 15 are not interconvertible without breakage and reunion of some chemical bonds. On the other hand, 1 and 2 in this chapter are interconvertible by the rotation about a single bond without breaking a bond. Such cases as 1 and 2 are referred to as having different conformations.

How can we distinguish conformations 1 and 2? Rotation about the C-C bond will cause a change in the dihedral angle $\phi$ and consequently the distance between HA and HB. If the distance between the two hydrogen atoms becomes short, the potential energy of the molecule will increase because the steric repulsion will have increased. When the dihedral angle $\phi = 0^\circ$, $120^\circ$ and $240^\circ$, it becomes maximal; when the dihedral angle $\phi = 60^\circ$, $180^\circ$ and $300^\circ$, it becomes minimal. Thus, the plot of $\phi$ and the potential energy will yield the dihedral angle-potential energy curve given in Fig. 2.3.

A study such as that of the change of molecular structure and energy caused by a rotation of the C-C (and other) single bond is called conformational analysis.

![Figure 2.3 Dihedral angle – energy diagram of ethane](image_url)

**S2.1 Conformational analysis**

conformational analysis: a study of the change of molecular structure (accompanied by the change of energy and properties) caused by a rotation about a single bond.

the dihedral angle-potential energy diagram: a plot of potential energy(abscissa) vs. dihedral angle (horizontal); indispensable for conformational analysis of simple molecules.

Potential energy of ethane is maximal when $\phi = 0^\circ$, $120^\circ$ and $240^\circ$, and minimal when $\phi = 60^\circ$, $180^\circ$ and $300^\circ$. The structure for the former is called staggered (4) and that for the latter eclipsed (3).

The potential energy difference between the two forms is ca. 12 kJ mol$^{-1}$ (2.86 kcal mol$^{-1}$). Conformations corresponding to the structures having minimal energy are called conformational isomers or simply conformers. In this book we use the word conformer throughout.

**S2.2 Eclipsed and staggered forms.**

eclipsed form 3: conformation of ethane and analogs with $\phi = 0^\circ$, $120^\circ$ and $240^\circ$

staggered form 4: conformation of ethane and analogs with $\phi = 60^\circ$, $180^\circ$ and $300^\circ
Q2.1
How many conformations does the ethane molecule have?

Q2.2
How many conformers does the ethane molecule have?

A2.1
Indefinite. By changing the dihedral angles minutely, you can obtain as many conformers as you like.

Q2.3
Do a conformational analysis of propane CH_3-CH_2-CH_3 and draw the dihedral angle-potential energy diagram. The dihedral angle is defined as the angle made by the C-CH_3 bond and the C-H bond.

A2.2
1. The conformers with $\phi = 60^\circ$, 180$^\circ$ and 300$^\circ$ are also identical.

A2.3
The dihedral angle-energy diagram will be much the same as Fig. 2.3. Since the CH_3---H interaction is necessarily larger than the H---H interaction, the energy difference between the staggered and eclipsed conformations is larger than that for ethane. Both curves have a similar cycle of 120$^\circ$. It must be mentioned that another C-C bond should also rotate and will cause a more complicated structural change. This process is not considered here.

2.3 Conformational analysis of butane

Although propane has much the same dihedral angle-energy diagram as that of ethane, a considerably different result will be obtained when conformational analysis of butane is done in relation to the rotation of the central C-C bond. When the potential energy of the molecule is plotted against the dihedral angle made by the two C-CH_3 bonds, there are obtained two forms with maximum energies (A and C of Fig. 2.4) and two conformers with minimum energies are obtained (B and D of Fig. 2.4).
Fig. 2.4 The dihedral angle-potential energy diagram of butane.

The Newman projection corresponding to forms A-D is shown below (5-8). In the case of ethane, the staggered and eclipsed conformations can sufficiently describe the features of its conformational analysis. In the case of butane, however, two conformations are not enough to describe the features of the diagram. The dihedral angle of one of the eclipsed forms, 5, is \( \phi = 0^\circ \). This form is called cis. The dihedral angle of the other staggered form, 6, is \( \phi = 60^\circ \). This form is called gauche. The other one, 8, with \( \phi = 180^\circ \) is called trans or anti.

Because of the proximity of two methyl groups, 5 and 6 have larger energies than 7 and 8, respectively. Cases will be discussed later where this treatment is not applicable because of more complicated structures.

\[
\begin{align*}
\phi = 0 & \quad 5 \\
60 & \quad 6 \\
120 & \quad 7 \\
180 & \quad 8
\end{align*}
\]

S2.3 Gauche and anti forms.

\textit{gauche} form: conformation of 1,2-disubstituted ethanes with \( \phi = 60^\circ \) (or \( 300^\circ \)).

\textit{anti(trans)} form: conformation of 1,2-disubstituted ethanes with \( \phi = 180^\circ \).

One can draw many Newman projections for a given molecule. For an ethane derivative ABC-CCDEF, projection can be done either from the ABC side (16) or from the DEF side (15). In addition, there are many rotational isomers (rotamers) in relation to the rotation about the C-C bond. Much the same is true for perspective drawings (11)-(14).

**Q2.4**

How many conformers are drawn (in different ways) with the perspective method (11-14) or Newman projection?
(a) 2 (11 = 13, 12 = 14), (b) 3 (15 = 16)

Nevertheless, we should not jump to the conclusion that we can separate the two conformers of butane in the ratio that we calculated. In order to isolate two interconvertible compounds such as 6 and 8 at room temperature, the energy barrier of interconversion (the energy difference between 6 and 8 or 5 and 7 in the case of butane) should be at least 100 kJ mol⁻¹.

As you can guess from Fig. 2.4, the actual energy difference is at most 15-20 kJ mol⁻¹. The interconversion takes place freely at room temperature.

### 2.4 Relative abundance of conformers

Ethane has two conformers; eclipsed and staggered. Does then ethane consist of two equal amounts of these two conformers? Definitely no. There are many other species with a different conformation. Furthermore, the two conformers have different steric energy, and hence the relative population of the two conformers may be different.

This situation can be visualized if we assume that the dihedral angle-energy diagram is a kind of reaction profile, which is a plot of the energy change of the system associated with the progress of the reaction. The vertical coordinate of a reaction profile, the reaction coordinate, corresponds to the dihedral angle of a dihedral angle-energy diagram. The eclipsed form is equivalent to the activated complex of a chemical reaction. Such a high-energy species will have a very short lifetime, and in almost all cases, it is impossible to isolate that species. In addition to the case of ethane, the eclipsed form for propane and butane is an intermediate of a reaction that has a very short lifetime.

One can assume that ethane exists most of the time as the most stable staggered form. In the case of butane there are two staggered forms, and hence it exists as a mixture of these two staggered forms. In such a case the relative amounts of the two staggered forms will depend on the difference in the Gibbs free energies ΔG. Generally speaking, for an equilibrium A ⇄ B, ΔG is expressed by the following equation

\[
ΔG = -2.303 \, RT \log K
\]

where \( K \) is the equilibrium constant (\( K = [B]/[A] \)), \( R \) the gas constant (\( = 1.98 \text{ cal deg}^{-1} \text{ mol}^{-1} \)) and \( T \) the absolute temperature.

\[ \text{S2.4 } ΔG \text{ and the relative amounts. The relation between the value of } ΔG \text{ and the population of} \]
conformers A and B are tabulated below.

<table>
<thead>
<tr>
<th>K (298K)</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>100</th>
<th>1000</th>
<th>10000</th>
</tr>
</thead>
<tbody>
<tr>
<td>amount of the more stable isomer(%)</td>
<td>67</td>
<td>75</td>
<td>80</td>
<td>83</td>
<td>91</td>
<td>95</td>
<td>99</td>
<td>99.9</td>
<td>99.99</td>
</tr>
<tr>
<td>∆G (kJ mol⁻¹)</td>
<td>1.71</td>
<td>2.72</td>
<td>3.43</td>
<td>3.97</td>
<td>5.85</td>
<td>7.52</td>
<td>11.3</td>
<td>17.1</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Q2.5
Suppose we can consider that the difference of potential energy between the gauche form and anti form of butane is approximately equal to the difference of free energy. Calculate the population of the two conformers at the room temperature (25°C).

Q2.6
If the difference in potential energy between the gauche form and the anti form of butane is higher than 100 kJ mol⁻¹, we should be able to isolate the more stable butane conformer at room temperature. How many varieties of conformers may be isolated? Guess the relation of their structures.

A2.5
From Fig. 2.4, the difference of free energy is 4 kJ mol⁻¹, which is equal to (4 x 10³/4.18) cal mol⁻¹. We can then obtain the following equation by substituting appropriate values into the equation given above.

\[
(4 \times 10^3/4.18) \text{(cal mol}^{-1}) = -2.303 \times 1.98 \text{(cal deg}^{-1} \text{mol}^{-1}) \times 298 \text{(deg)} \log K
\]

\[
\therefore \log K = 0.692; K = 4.95
\]

If we take the molar ratio of the gauche form as \(x\), then \((1 - x)/x = 4.95; x = 0.168\)

Finally, we can conclude that the anti form is ca. 17% and the gauche form ca. 83%, which is in qualitative agreement with our prediction.

This does not, however, mean that one can separate butane into the anti and gauche forms. In order to separate at room temperature two rapidly exchanging species, e.g., 6 and 8, the barrier for the exchange, in the case of butane, the energy difference between 6 and 8 or 5 and 7, should be at least as large as 100 kJ mol⁻¹. As is indicated in Fig. 2.4, the energy difference is ca. 15-20 kJ mol⁻¹, indicating that at room temperature the exchange is very rapid and separation is impossible.

A2.6
3; 6, 8 and 19 (\(\phi = 270°\)). All are conformers of one another. You should confirm, with the aid of the molecular model, that 6 and 19 are not identical but enantiomers each other.

2.5 Stereochemical nomenclature of ethane derivatives

We have already learned several terms, such as gauche, anti, staggered or eclipsed, to name the conformers based on the Newman projection. These are, however, insufficient when a more complex molecule is involved. For instance, there are three staggered forms for 2,3-dimethylbutane as shown below. It is impossible to define these as gauche or anti as long as we use the relations of methyl groups as the standard.
A systematic nomenclature has been proposed which could be applicable to such complex cases. For a four-atom system A-C₁-C₂-B, a torsion angle $\theta$ (23) is defined. Atoms C₁ and C₂ may be other types of atoms, but for simplicity we take these two as carbon atoms.

The definition of torsion angle is as follows.
1) We look at the molecule along the C₁-C₂ axis as shown in 23.
2) Rotate the A-C₁ bond so that A overlaps B.
3) The torsion angle is defined as the angle of rotation necessary to overlap A with B.
4) The torsion angle is positive if the required rotation is clockwise, and negative if the rotation is counterclockwise.

It is important to notice that the torsion angle has a sign though the dihedral angle does not. Hereafter we shall use the torsion angle as far as possible in this textbook.

Ligands A and B are chosen from the ligands bonded to C₁ and C₂, respectively.
1) If all three ligands are different, the priority is determined by the sequence rule.
2) If two ligands are identical, the rest are chosen for A and B regardless of the priority based on the sequence rule.
3) If three ligands are identical, the one associated with the smallest torsion angle is chosen.

In practice, the torsion angle of ethane derivatives is not necessarily a multiple of 60°. Hence, the value of the torsion angle itself is not included in the stereochemical names. A circle (torsion angle = 360°) is divided into several sections as is shown in 24-26, and each section is given a name. By combining these names, a system of nomenclature of ethane derivatives is established.

The upper half of the circle is syn region, and the lower half is anti region (cf. 25). The p of 26 stands for the periplanar region, and c for the clinal region. By combining these regions, you can obtain 27.

The essentials of this nomenclature will be summarized in S2.5.

**S2.5** The stereochemical nomenclature based on the rotation about a single bond.
<table>
<thead>
<tr>
<th>torsion angle $\theta$</th>
<th>name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0 \pm 30^\circ$</td>
<td>$\pm$synperiplanar ($\pm sp$)</td>
</tr>
<tr>
<td>$\pm 30^\circ \sim +90^\circ$</td>
<td>$+$synclinal ($+sc$)</td>
</tr>
<tr>
<td>$+ 90^\circ \sim +150^\circ$</td>
<td>$+$anticlinal ($+ac$)</td>
</tr>
<tr>
<td>$+ 150^\circ \sim +180^\circ$</td>
<td>$+$antiperiplanar ($+ap$)</td>
</tr>
<tr>
<td>$- 30^\circ \sim -90^\circ$</td>
<td>$-$synclinal ($-sc$)</td>
</tr>
<tr>
<td>$- 90^\circ \sim -150^\circ$</td>
<td>$-$anticlinal ($-ac$)</td>
</tr>
<tr>
<td>$-150^\circ \sim -180^\circ$</td>
<td>$-$antiperiplanar ($-ap$)</td>
</tr>
</tbody>
</table>

**Q2.7**

Compounds 28 ~ 31 have two halogen atoms as substituents. Define the conformation of each compound in terms of (a) staggered – eclipsed and (b) $sp$, $ap$, etc.

![Compounds 28 to 31](image)

**Q2.8**

Define the conformation of the two compounds shown below.

![Compounds 32 and 33](image)

**A2.7**

28 *eclipsed, $\pm sp$,* 29 *staggered, $+sc$*, 30 *staggered, $\pm ap$* (you may answer simply $ap$) 31 *eclipsed $-ac$.*

**Q2.9**

Define the conformation of all conformers of butane 5~8, and two isomers with $\theta = -60^\circ$ and $-120^\circ$, in terms of $sp$, $ac$, etc.

**A2.8**

32 *$+sc$* (Ph and OH are the reference ligands.)

33 *$+sc$* (H (not Ph) and OH are the reference ligands.)

9(10)
Q2.10
Sketch the torsion angle-energy diagram (like Figs. 2.3 and 2.4) of 2,3-dimethylbutane. Show the Newman projection of the relevant conformer when the energy is maximal or minimal.

A2.9

<table>
<thead>
<tr>
<th>Compound</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>(-60°)</th>
<th>(-120°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ</td>
<td>0°</td>
<td>60°</td>
<td>120°</td>
<td>180°</td>
<td>240°</td>
<td>300°</td>
</tr>
<tr>
<td>name</td>
<td>±sp</td>
<td>+sc</td>
<td>+ac</td>
<td>±ap</td>
<td>-ac</td>
<td>-sc</td>
</tr>
</tbody>
</table>

A2.10

The energy barrier for the interconversion $21 \rightarrow 20 \rightarrow 22$ is ca. 18 kcal mol$^{-1}$, and that for the interconversion $21 \rightarrow \pm sp \rightarrow 22$ is ca. 33 kcal mol$^{-1}$. 