Objectives

After completing this section, you should be able to

1. describe the Baeyer strain theory.
2. describe how the measurement of heats of combustion provides information about the amount of strain present in a cycloalkane ring.
3. determine the relative stability of cyclic compounds, by assessing such factors as angle strain, torsional strain and steric strain.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- angle strain
- steric strain
- torsional strain
- ring strain
- heat of combustion

Heat of Combustion

The combustion of carbon compounds, especially hydrocarbons, has been the most important source of heat energy for human civilizations throughout recorded history. The practical importance of this reaction cannot be denied, but the massive and uncontrolled chemical changes that take place in combustion make it difficult to deduce mechanistic paths. Using the combustion of propane as an example, we see from the following equation that every covalent bond in the reactants has been broken and an entirely new set of covalent bonds have formed in the products. No other common reaction involves such a profound and pervasive change, and the mechanism of combustion is so complex that chemists are just beginning to explore and understand some of its elementary features.

\[
\text{CH}_3\text{CH}_2\text{CH}_3 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} + \text{Heat}
\]

Since all the covalent bonds in the reactant molecules are broken, the quantity of heat evolved in this reaction, and any other combustion reaction, is related to the strength of these bonds (and, of course, the strength of the bonds formed in the products). Precise heats of combustion measurements can provide useful information about the structure of molecules and their relative stability.

For example, heat of combustion is useful in determining the relative stability of isomers. Pentane has a heat of combustion of $-782$ kcal/mole, while that of its isomer, 2,2-dimethylpropane (neopentane), is $-777$ kcal/mole. These
values indicate that 2,3-dimethylpentane is 5 kcal.mole more stable than pentane, since it has a lower heat of combustion.

Ring Strain

Table 4.3.1 lists the heat of combustion data for some simple cycloalkanes. These cycloalkanes do not have the same molecular formula, so the heat of combustion per each CH$_2$ unit present in each molecule is calculated (the fourth column) to provide a useful comparison. From the data, cyclopropane and cyclobutane have significantly higher heats of combustion per CH$_2$, while cyclohexane has the lowest heat of combustion. This indicates that cyclohexane is more stable than cyclopropane and cyclobutane, and in fact, that cyclohexane has a same relative stability as long chain alkanes that are not cyclic. What causes this difference in stability or the strain in these two small cycloalkanes?

<table>
<thead>
<tr>
<th>Cycloalkane (CH$_2$)$_n$</th>
<th>CH$_2$ Units $n$</th>
<th>$\Delta H^{25^\circ}$ kcal/mole</th>
<th>$\Delta H^{25^\circ}$/ per CH$_2$ Unit</th>
<th>Ring Strain kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropane</td>
<td>n = 3</td>
<td>468.7</td>
<td>156.2</td>
<td>27.6</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>n = 4</td>
<td>614.3</td>
<td>153.6</td>
<td>26.4</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>n = 5</td>
<td>741.5</td>
<td>148.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>n = 6</td>
<td>882.1</td>
<td>147.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>n = 7</td>
<td>1035.4</td>
<td>147.9</td>
<td>6.3</td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>n = 8</td>
<td>1186.0</td>
<td>148.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Cyclononane</td>
<td>n = 9</td>
<td>1335.0</td>
<td>148.3</td>
<td>11.7</td>
</tr>
<tr>
<td>Cyclodecane</td>
<td>n = 10</td>
<td>1481</td>
<td>148.1</td>
<td>11.0</td>
</tr>
<tr>
<td>CH$_3$(CH$_2$)$_m$CH$_3$</td>
<td>m = large</td>
<td>—</td>
<td>147.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The Baeyer Theory on the Strain in Cycloalkane Rings

In 1890, the famous German organic chemist, A. Baeyer, suggested that cyclopropane and cyclobutane are less stable than cyclohexane, because the smaller rings are more “strained”. There are many different types of strain that
contribute to the overall ring strain in cycloalkanes, including angle strain, torsional strain, and steric strain. **Torsional strain** and **steric strain** were previously defined in the discussion of conformations of butane. **Angle Strain** occurs when the sp$^3$ hybridized carbons in cycloalkanes do not have the expected ideal bond angle of 109.5°, causing an increase in the potential energy. An example of angle strain can be seen in the diagram of cyclopropane below in which the bond angle is 60° between the carbons.

![cyclopropane.bmp](attachment:image1)

The C-C-C bond angles in cyclopropane (diagram above) (60°) and cyclobutane (90°) are much different than the ideal bond angle of 109.5°. This bond angle causes cyclopropane and cyclobutane to be less stable than molecules such as cyclohexane and cyclopentane, which have a much lower ring strain because the bond angle between the carbons is much closer to 109.5°. Changes in chemical reactivity as a consequence of angle strain are dramatic in the case of cyclopropane, and are also evident for cyclobutane.

In addition to angle strain, there is also steric (transannular) strain and torsional strain in many cycloalkanes. Transannular strain exists when there is steric repulsion between atoms. Torsional (eclipsing) strain exists when a cycloalkane is unable to adopt a staggered conformation around a C-C bond. Torsional strain and steric strain are especially prevalent in small cycloalkanes whose structures are nearly planar.

Larger rings like cyclohexane, deal with torsional strain by forming **conformers** in which the rings are not planar. A conformer is a stereoisomer in which molecules of the same connectivity and formula exist as different isomers, in this case, to reduce ring strain. The ring strain is reduced in conformers due to the rotations around the sigma bonds, which decreases the angle and torsional strain in the ring. The non-planar structures of cyclohexane are very stable compared to cyclopropane and cyclobutane, and will be discussed in more detail in the next section.

![transannular strain.bmp](attachment:image2)
Exercises

Questions

Q4.3.1

trans-1,2-Dimethylcyclobutane is more stable than cis-1,2-dimethylcyclobutane. Explain this observation.

Solutions

S4.3.1

The trans form does not have eclipsing methyl groups, therefore lowering the energy within the molecule. It does however have hydrogen-methyl interactions, but are not as high in energy than methyl-methyl interactions.

Contributors

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Objectives

After completing this section, you should be able to

1. describe, and sketch the conformation of, cyclopropane, cyclobutane and cyclopentane.
2. describe the bonding in cyclopropane, and hence account for the high reactivity of this compound.
3. analyse the stability of cyclobutane, cyclopentane and their substituted derivatives in terms of angular strain, torsional strain and steric interactions.

Study Notes

Notice that in both cyclobutane and cyclopentane, torsional strain is reduced at the cost of increasing angular (angle) strain.

Although the customary line drawings of simple cycloalkanes are geometrical polygons, the actual shape of these compounds in most cases is very different.

Cyclopropane is necessarily planar (flat), with the carbon atoms at the corners of an equilateral triangle. The 60° bond angles are much smaller than the optimum 109.5° angles of a normal tetrahedral carbon atom, and the resulting angle strain dramatically influences the chemical behavior of this cycloalkane. Cyclopropane also suffers substantial eclipsing strain, since all the carbon-carbon bonds are fully eclipsed. Cyclobutane reduces some bond-eclipsing strain by folding (the out-of-plane dihedral angle is about 25°), but the total eclipsing and angle strain remains high. Cyclopentane has very little angle strain (the angles of a pentagon are 108°), but its eclipsing strain would be large (about 10 kcal/mol) if it remained planar. Consequently, the five-membered ring adopts non-planar puckered conformations whenever possible.

Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring).

Cyclic systems are a little different from open-chain systems. In an open chain, any bond can be rotated 360 degrees, going through many different conformations. That complete rotation isn't possible in a cyclic system, because the parts that would be trying to twist away from each other would still be connected together. Cyclic systems have fewer "degrees of freedom" than aliphatic systems; they have "restricted rotation".

Because of the restricted rotation of cyclic systems, most of them have much more well-defined shapes than their aliphatic counterparts. Let's take a look at the basic shapes of some common rings.

- Many biologically important compounds are built around structures containing rings, so it's important that we become familiar with them.
In nature, three- to six-membered rings are frequently encountered, so we'll focus on those.

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**Cyclopropane**

A three membered ring has no rotational freedom whatsoever. A plane is defined by three points, so the three carbon atoms in cyclopropane are all constrained to lie in the same plane.

Furthermore, if you look at a model you will find that the neighboring C-H bonds (C-C bonds, too) are all held in eclipsed conformations.

Cyclopropane is always at maximum torsional strain. This strain can be illustrated in a line drawing of cyclopropane as shown from the side. In this oblique view, the dark lines mean that those sides of the ring are closer to you.

However, the ring isn't big enough to introduce any steric strain, which does not become a factor until we reach six membered rings. Until that point, rings are not flexible enough for two atoms to reach around and bump into each other.

The really big problem with cyclopropane is that the C-C-C bond angles are all too small.

- All the carbon atoms in cyclopropane appear to be tetrahedral.
- These bond angles ought to be 109 degrees.
- The angles in an equilateral triangle are actually 60 degrees, about half as large as the optimum angle.
- This factor introduces a huge amount of strain in the molecule, called angle strain. The large amount of ring strain in cyclopropane weakens the bonds and causes cyclopropane to be significantly more reactive than expected for a hydrocarbon molecule.

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**Cyclobutane**

Cyclobutane is a four membered ring. In two dimensions, it is a square, with 90 degree angles at each corner.

However, in three dimensions, cyclobutane is flexible enough to buckle into a "butterfly" shape, relieving torsional strain a little bit. When it does that, the bond angles get a little worse, going from 90 degrees to 88 degrees.
In a line drawing, this butterfly shape is usually shown from the side, with the near edges drawn using darker lines.

- Angle strain is significant. With bond angles of 88 rather than 109 degrees, cyclobutane has a lot of angle strain, but less than in cyclopropane.
- Torsional strain is still present, but the neighboring bonds are not exactly eclipsed in the butterfly.
- Steric strain is very low. Cyclobutane is still not large enough that the molecule can reach around to cause crowding.
- Cyclobutanes are a slightly more stable than cyclopropanes and are also a little more common in nature.

**Cyclopentane**

Cyclopentanes are even more stable than cyclobutanes, and they are the second-most common cycloalkane ring in nature, after cyclohexanes. In two dimensions, a cyclopentane appears to be a regular pentagon.

In three dimensions, there is enough freedom of rotation to allow a slight twist out of this planar shape. In a line drawing, this three-dimensional shape is drawn from an oblique view, just like cyclobutane.

- Angle strain is low. The ideal angle in a regular pentagon is about 107 degrees, very close to a tetrahedral bond angle.
- There is still some torsional strain in cyclopentane. Cyclopentane distorts only very slightly into an "envelope" shape in which one corner of the pentagon is lifted up above the plane of the other four. The envelope removes torsional strain along the sides and flap of the envelope. However, the neighboring carbons are eclipsed along the "bottom" of the envelope, away from the flap.
- Again, there is no steric strain in this system.
Exercises

Questions

Q4.4.1
If cyclobutane were to be planar how many H-H eclipsing interactions would there be, and assuming 4 kJ/mol per H-H eclipsing interaction what is the strain on this “planar” molecule?

Q4.4.2
In the two conformations of cis-cyclopentane one is more stable than the other. Explain why this is.

Solutions

S4.4.1
There are 8 eclipsing interactions (two per C-C bond). The extra strain on this molecule would be 32 kJ/mol (4 kJ/mol x 8).

S4.4.2
The first conformation is more stable. Even though the methyl groups are cis in the model on the left, they are eclipsing due the conformation, therefore increasing the strain within the molecule.

Contributors

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