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
In nature, three- to six-membered rings are frequently encountered, so we'll focus on those.

**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.

![Cyclopropane](image)

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.

**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.

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**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.

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**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.

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