Conformations of Rings

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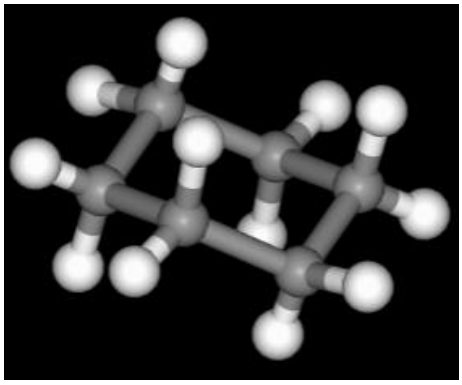


1 Introduction

In 1885 Adolf von Baeyer proposed that if carbon prefers to have a tetrahedral geometry with bond angles of 109.5°, then ring sizes other than 5 and 6 may be too strained to exist. The basis for this proposal was that all ring system are planar. Clearly, this is not the case. Ring systems can adopt many different conformations just as acyclic compounds do. The Cambridge Structural Database is a unique resource providing a wealth of information on the preferred conformations of rings. Indeed, the database has been used extensively to map the conformational space of medium ring-sized cyclic and heterocyclic compounds[1] and of macrocyclic ether and thioether ligands.[2] By examining crystal structures we can understand why the observed conformations are adopted in terms of the strain present in these systems.

1.1 Learning outcomes

At the end of this module, you will:

- understand the reason for angle strain in fully saturated planar carbocyclic rings
- know how to determine the angle strain in molecules in experimental crystal structures
- be able to account for differences between predicted angle strain of planar rings and the values from actual compounds
- understand the conformations of 3- to 6-membered rings in terms of the strain present in these systems.

1.2 Materials

The structures needed to complete this module are available from the online Web service Access Structures.

https://www.ccdc.cam.ac.uk/structures/

This provides you with all the features required to complete this teaching module. Alternatively, you may prefer to use the structure visualization program Mercury, which you can download for free. Instructions for obtaining this software and links to resources to support you using it are given at the end of this document. This teaching module uses entries in the Teaching Subset; you can find out more about the Teaching Subset here: https://www.ccdc.cam.ac.uk/community/education-and-outreach/education/teaching-subset/.

1.3 Pre-requisite skills

No prior knowledge of crystallography is required to complete this teaching module. Basic familiarity with molecular structure is assumed.

[1] F. H. Allen, J. A. K. Howard and N. A. Pitchford, *Acta Cryst.*, B**49**, 1993, 910–928, DOI: 10.1107/S0108768193004896

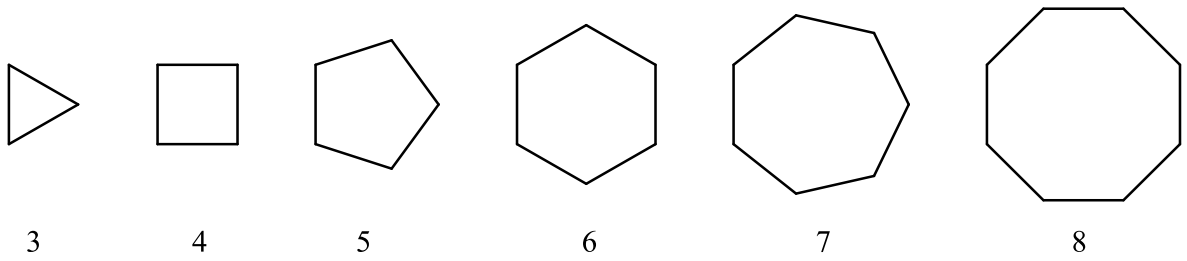
[2] *Acta Cryst.*, B**53**, 1997, 241-251, DOI: 10.1107/S0108768196013663

2 Introduction to Ring Conformations

2.1 Investigating angle strain in planar rings

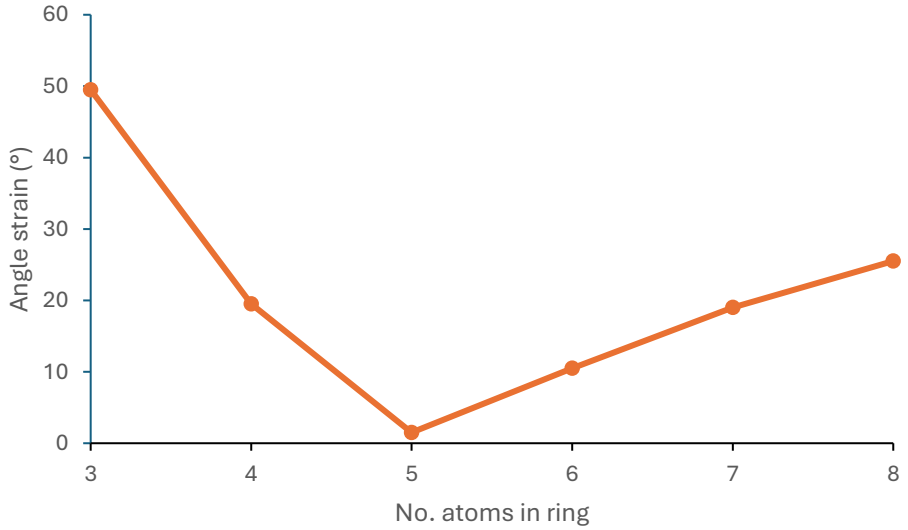
Ideally the sp^3 hybridised carbon atoms of fully saturated carbocyclic rings would adopt bond angles of 109.5°. However, in planar rings the internal bond angles will depend on the number of atoms in the ring.

1. Complete the table below to calculate the angle strain for the specified planar ring sizes using the formula $angle\ strain = |internal\ angle - 109.5|$



No. atoms in ring	Internal angle in planar structure (°)	Angle strain (°)
3	60	49.5
4	90	19.5
5	108	1.5
6	120	
7	128.5	
8	135	

2. Plot the data as graph of angle strain vs number of atoms in the ring. You should find it looks like the graph below. What conclusions can you draw?



Strain is predicted to be largest for 3-membered rings but rapidly decreases and reaches a minimum for a 5-membered ring. In fact, a planar 5-membered ring is predicted to be virtually free of angle strain. After the minimum at five, angle strain increases steadily as the rings get larger.

2.2 Calculating angle strain in experimental structures

So far we only have a predicted value of angle strain in planar rings. We need a measure of angle strain in the actual molecules, so that we can compare this to the predicted values. The preferred angle in actual compounds can be determined, for an *n*-membered carbocyclic ring, by taking the average internal angle across a large number crystal structures. Angle strain can then be calculated as the difference between this average internal angle and the ideal sp^3 angle of 109.5°.

We will begin by calculating the angle strain in cyclohexane by measuring the internal angles of the cyclohexane rings in selected molecules.

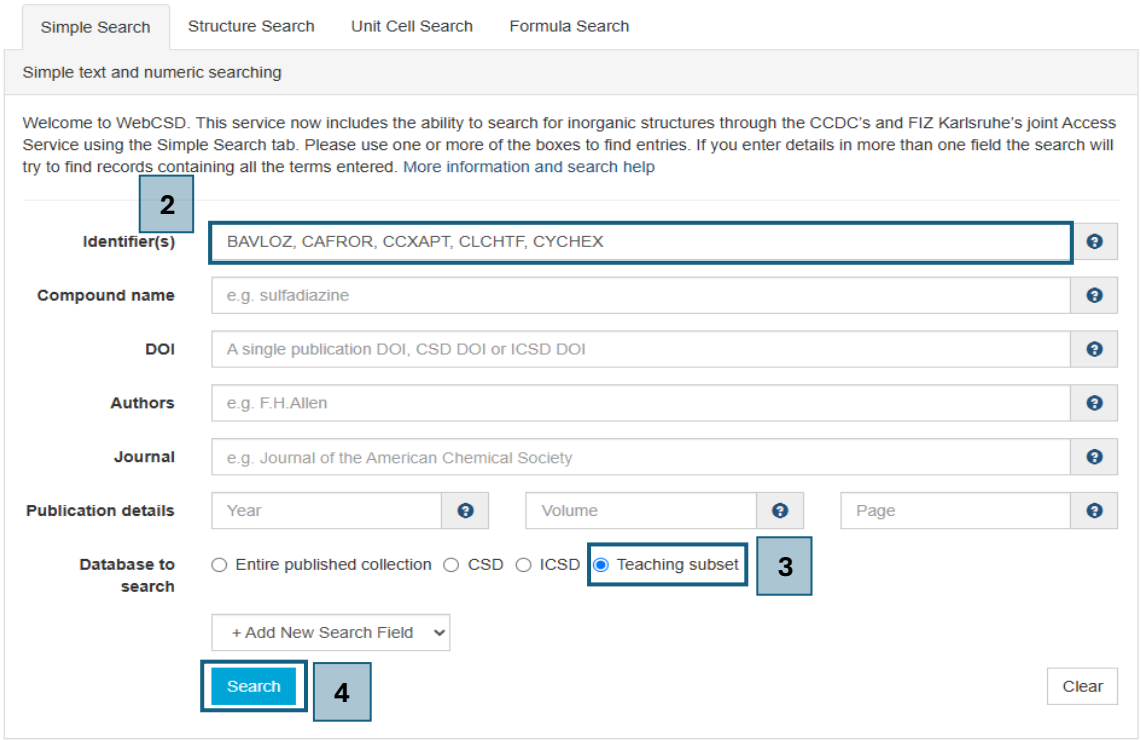
Access Structure can be used to view 3D structures and take angle measurements.

1. In a web browser, navigate to Access Structures www.ccdc.cam.ac.uk/structures/ .

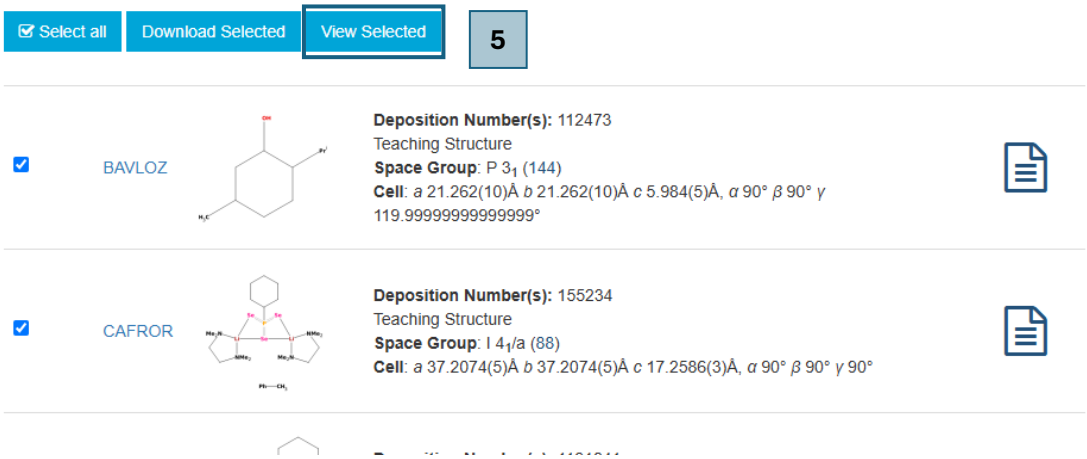
2. In the Simple search tab, type "BAVLOZ, CAFROR, CCXAPT, CLCHTF, CYCHEX" into the *Identifiers* field (you can omit the commas if you wish).

3. Select **Teaching Subset** from the *Database to search* options.

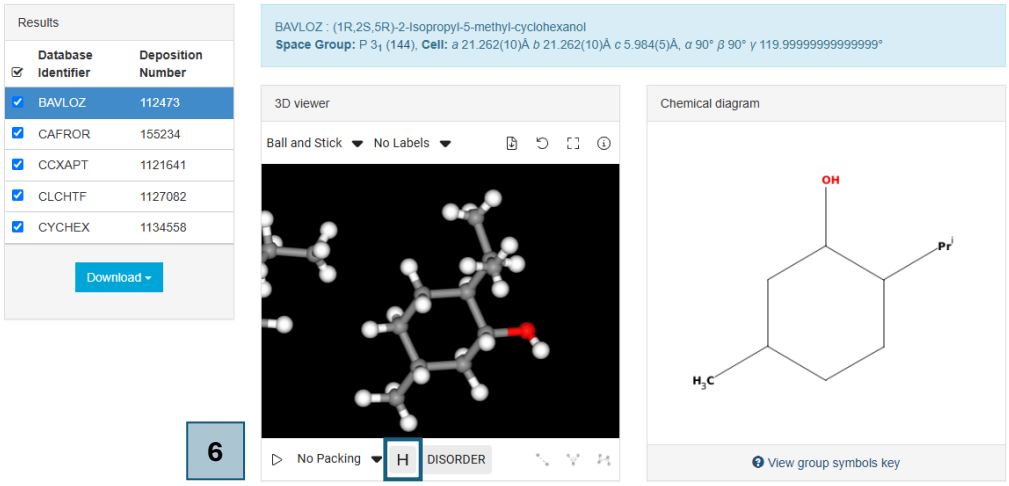
4. Press **Search**.



5. In the results page, make sure all entries are selected (if they are not, press **Select all**) and click View Selected.

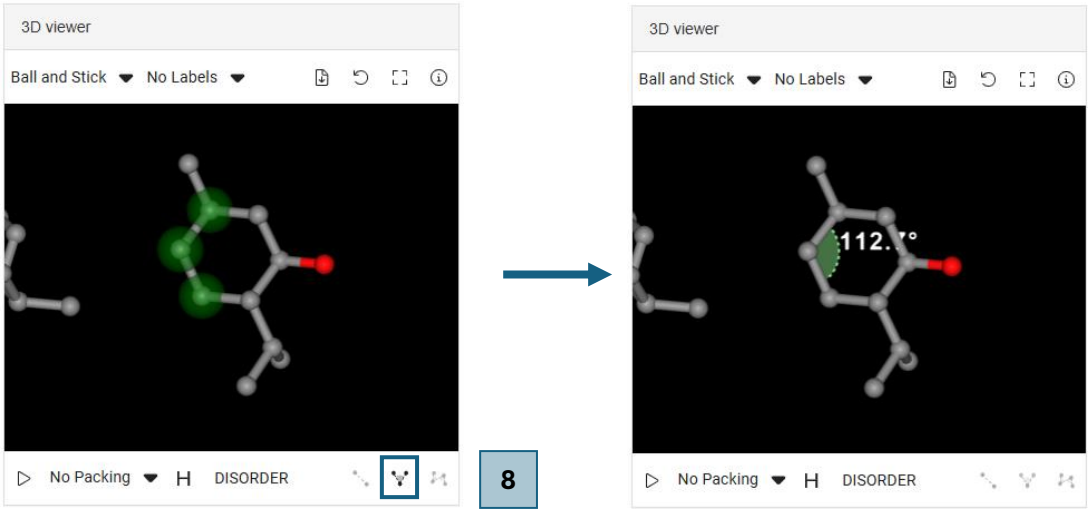


6. The details of the first hit will be displayed. The 6-letter code (BAVLOZ in this case) is a CSD database identifier which we refer to as a refcode. You can move between hits by selecting them from the *Results* panel. The 3D structure will be loaded in the 3D viewer. To make the view clearer, you might wish to turn off the display of hydrogen atoms using the **H** button.



7. To manipulate the structure:
   - Left click and drag to rotate the structure.
   - Right click and drag to translate the structure.
   - Scroll up/down with the mouse wheel to zoom in/out.
   - At any time, hit ↺ to reset the viewer.

8. Click on any three adjacent atoms in a cyclohexane ring (there are three molecules in BAVLOZ, we suggest picking just one). They will be highlighted in green translucent spheres. Click on the icon to measure the angle. If you have time, you could do the same for the other molecules.



9. Repeat this process for the remaining bond angles in the cyclohexane ring and then apply the same analysis to all refcodes searched. Record your measurements in the table overleaf.

Refcode	**Internal C–C–C angles (°)**	**Average internal C–C–C angle (°)**
BAVLOZ (pick one molecule)	Angle 1:	
	Angle 2:	
	Angle 3:	
	Angle 4:	
	Angle 5:	
	Angle 6:	
CAFROR	Angle 1:	
	Angle 2:	
	Angle 3:	
	Angle 4:	
	Angle 5:	
	Angle 6:	
CCXAPT (pick one ring)	Angle 1:	
	Angle 2:	
	Angle 3:	
	Angle 4:	
	Angle 5:	
	Angle 6:	
CLCHTF	Angle 1:	
	Angle 2:	
	Angle 3:	
	Angle 4:	
	Angle 5:	
	Angle 6:	

Refcode	Internal C-C-C Angles	Average Internal C-C-C Angle
CYCHEX	Angle 1:	
	Angle 2:	
	Angle 3:	
	Angle 4:	
	Angle 5:	
	Angle 6:	
Average internal C-C-C angle over whole set:		

Note that we have used only a small number of representative structures in this exercise, however, if you have full CSD access you can calculate this angle across a wide range of angles.

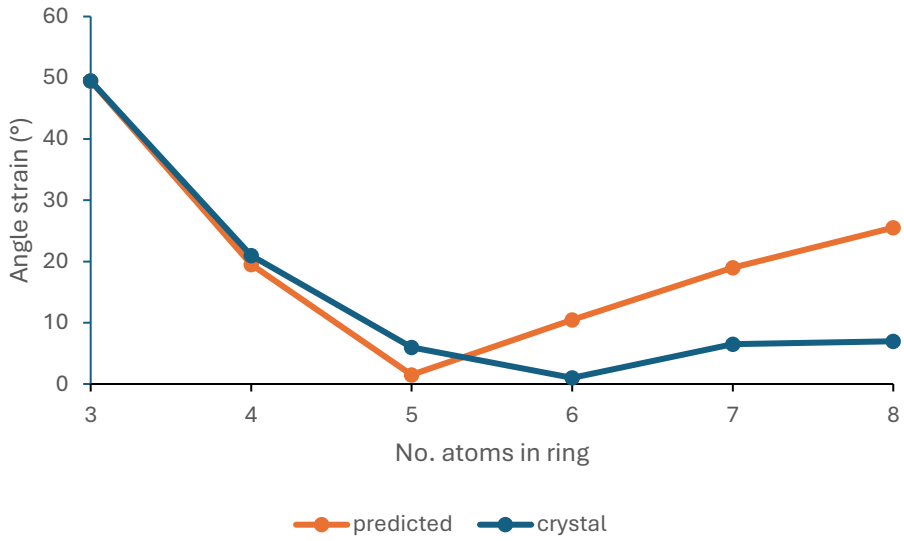
2.3 Comparing predicted and experimental angle strain

The table below shows both the predicted angle strain (in planar rings) and the angle strain calculated from actual compounds.

1. Complete the table by entering the angle strain in cyclohexane calculated from the crystal structures in Section 2.2. Your answer should be close to zero.

No. atoms in ring	**Strain angle (°)**	
	Predicted (in planar rings)	Calculated (crystal structure data)
3	49.5	49.5
4	19.5	21
5	1.5	6
6	10.5	
7	19	6.5
8	25.5	7

2. Add the strain angle data to the graph plotted in Section 2.1. This will allow us to easily compare the predicted values with measurements from the crystal structures. The graph should appear as shown overleaf.



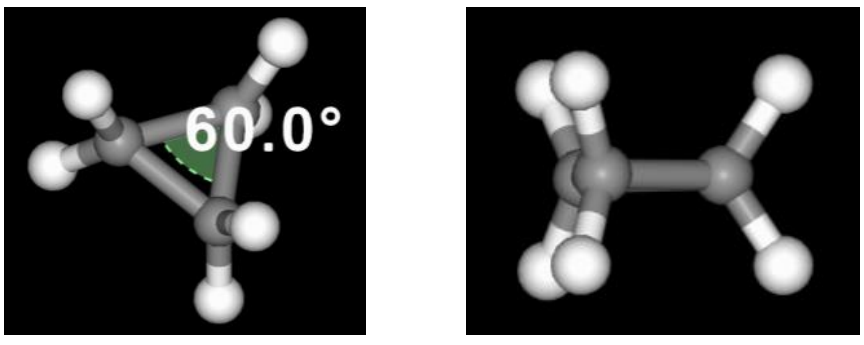
Comparing the two data series, the observed angle strain is greatest in cyclopropane. Angle strain then decreases rapidly with ring size but reaches a minimum for cyclohexane, not cyclopentane (as predicted for the planar structure). Angle strain then increases again but not nearly as quickly as predicted.

Why are 6-membered rings essentially free of angle strain? and why is there some angle strain in five membered rings even though the bond angles in the planar structure are almost 109.5°? The answer, at least to the first question, is that rings in actual compounds are not planar, they can adopt many different conformations just as acyclic compounds do. To help answer the second question, let's look at some ring conformations in more detail.

2.4 Ring conformations of cycloalkanes

Cyclopropane

Using Access Structures (www.ccdc.cam.ac.uk/structures) find cyclopropane, refcode QQQCIS01, and examine the structure. You will see that it is planar, as any 3-membered ring must be, and the internal angles are 60°. We know that cyclopropane has significant angle strain, but there is a further cause of strain in this molecule. Can you identify what this is? (*hint:* it may help to look along a C–C bond).



Left: the cyclopropane ring has high angle strain. Right: view of the eclipsing interactions.

All the C–H bonds in cyclopropane are eclipsed. This is energetically unfavourable and any rotation would lead to a more stable conformation. However, C-C bond rotation is impossible and so all the C–H bonds are forced to eclipse their neighbours. The strain resulting from eclipsed conformations is called torsional strain (also called eclipsing strain or Pitzer strain).

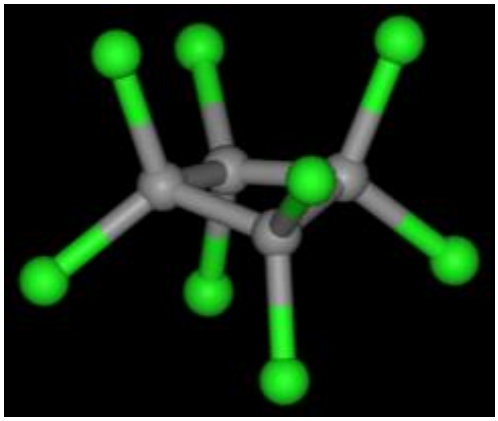
Cyclobutane

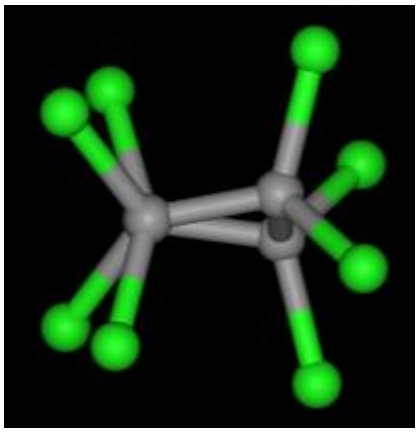
Cyclobutane itself is disordered, so we cannot extract reliable bond angle data from it. For an explanation of disorder, see:

https://www.ccdc.cam.ac.uk/media/Guide_to_the_Teaching_Subset.pdf

Instead, we shall look at octachlorocyclobutane, CSD refcode CLCBUT. Find this using Access Structures and examine the 3D structure.

In octachlorocyclobutane the ring distorts from a planar conformation in order to reduce the eclipsing interactions, even though this increases the angle strain. Octachlorocyclobutane therefore adopts a wing-shaped conformation, with an angle between the C–C–C planes of about 26° (measurements involving planes can be performed using the free visualiser Mercury; see https://www.ccdc.cam.ac.uk/media/HG-Measuring-Objects.pdf). The view along any of the C–C bonds reveals how the distortion relieves the eclipsing interaction.



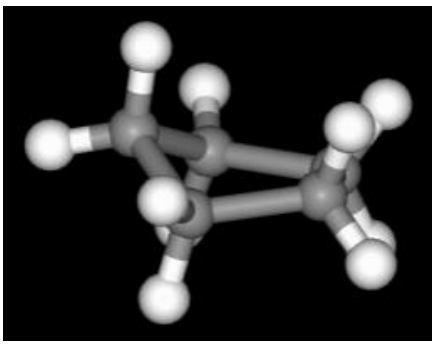


Left: the wing-shaped conformation of the cyclobutane ring. Right: view along a C–C bond.

By comparison, oxetane (CSD refcode CIVXIO10), in which eclipsing is less, is closer to planarity, with an angle of 10.8° between the C–C–C and C–C–O planes.

Cyclopentane

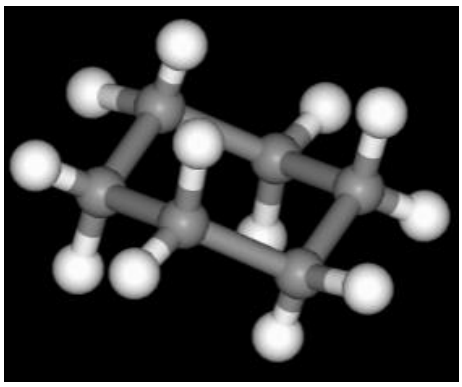
The eclipsing effect explains why there is some angle strain in 5-membered rings even though the bond angles in the hypothetical planar structure are close to the ideal value of 109.5°. As with cyclobutane, the structure distorts to reduce eclipsing interactions at the expense of creating some angle strain. The minimum energy conformation adopted is therefore a balance of the two opposing types of strain. There are two puckered conformations: envelope and half-chair. The energy difference between them is small and consequently 5-membered rings often adopt a conformation somewhere in between these extremes. Examine CSD refcode ZZZVYE01 in Access Structures. You will see that the conformation most closely resembles the envelope form.

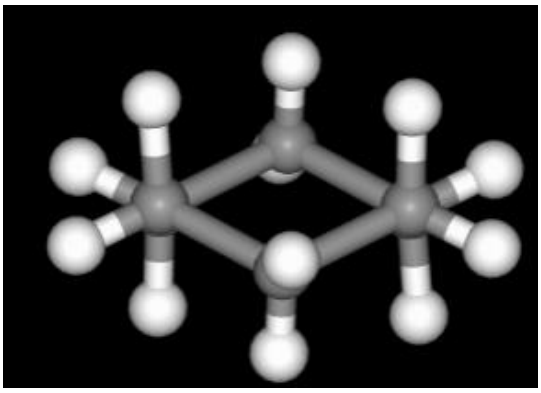


CSD entry ZZZVYE01 showing the envelope shape of cyclopentane.

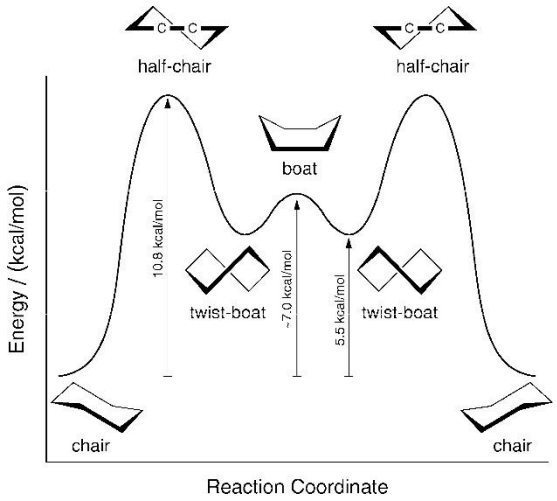
Cyclohexane

From our analysis of crystal structure data we have determined that 6-membered rings are essentially free of angle strain. Inspect the structure of cyclohexane (CSD refcode CYCHEX) and explain why this is so. Cyclohexane adopts a puckered conformation that relieves all strain, with bond angles close to 109.5° in the ring, and all bonds staggered, i.e. in a *gauche* arrangement, with respect to one another (no eclipsing interactions). This conformation is called the *chair*. In the vast majority of compounds, cyclohexane exists in the chair conformation. Other conformations are known but represent higher energy forms (see energy profile below) that are not typically seen in the solid state unless part of a fused ring system, such as in norbornane (CSD refcode QQQAPG02).





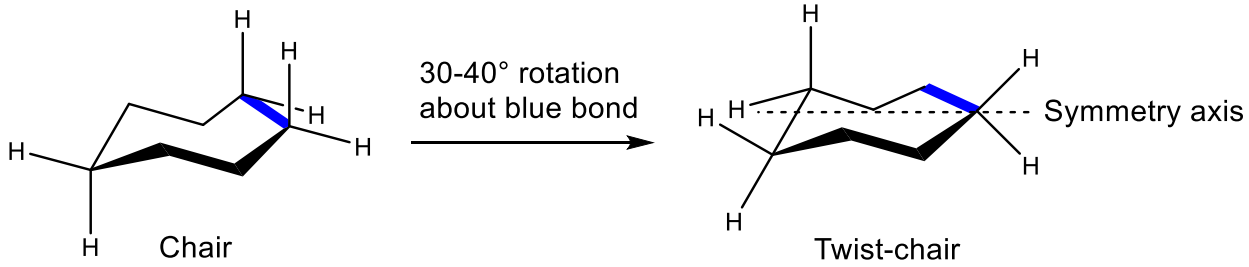
Left: the chair conformation of cyclohexane in CSD refcode CYCHEX. Right: a view of cyclohexane showing the bonds staggered with respect to one another.

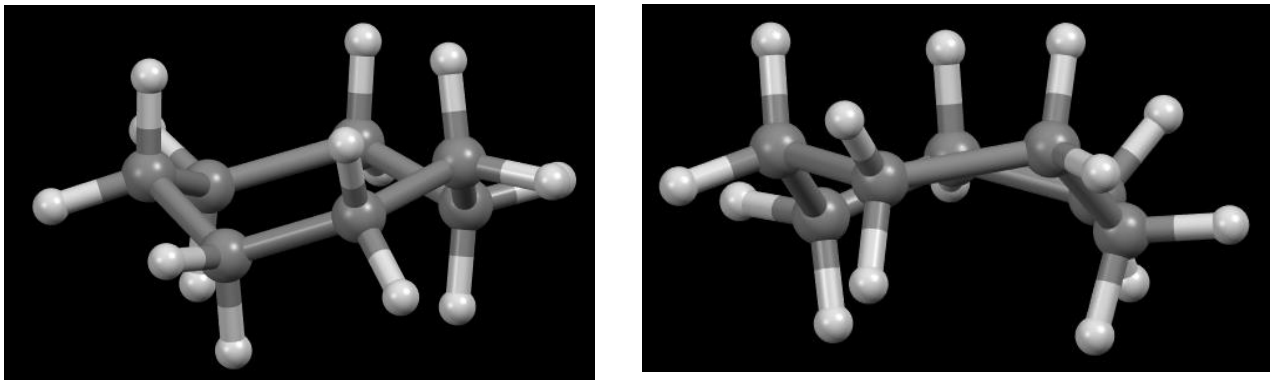


The energy profile of different cyclohexane conformations. Reprinted with permission from D. J. Nelson and C. N. Brammer, *J. Chem. Educ*., 2011, **88**, 3, 292–294. Copyright 2025 American Chemical Society.

Cycloheptane

Aliphatic rings with more than six atoms tend to be more flexible than smaller rings. Examples of cycloheptane without disorder in the CSD are rare, however, in CSD entry IYUZOT, you can find cycloheptane as a guest molecule encapsulated in a cage. You may need to open this in Mercury to hide the cage atoms to get a clearer view (see below). The shape can be described approximately as 'twist-chair'; it is the lowest energy conformation of cycloheptane, the next highest being the non-twisted chair.

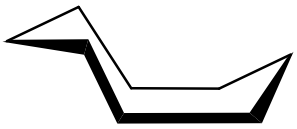




Different views of the cycloheptane guest molecule in IYUZOT.

Cyclooctane

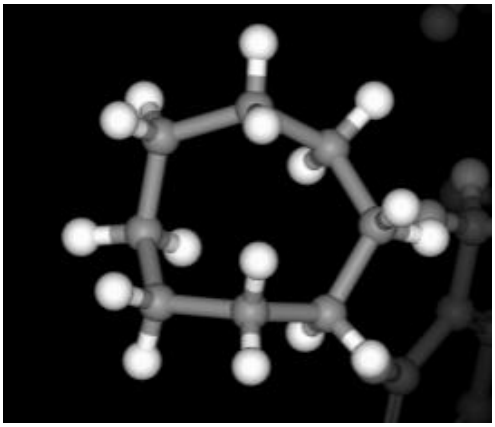
Much like cycloheptane, a number of different conformations are possible for cyclooctane, which include boat-chair, twist-boat-chair, crown, boat-boat and twist boat. The boat-chair and crown conformation are shown below for reference. They are generally present as mixtures whose conformational composition depends on temperature and phase (i.e. vapour, liquid etc.), however the boat-chair is found to be the dominant form regardless.

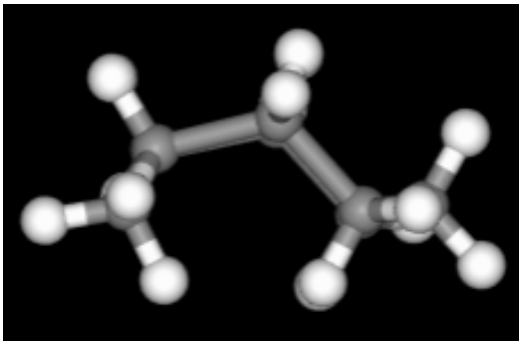


Boat-chair

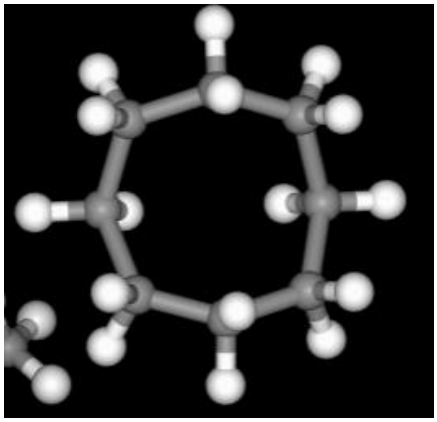
Crown

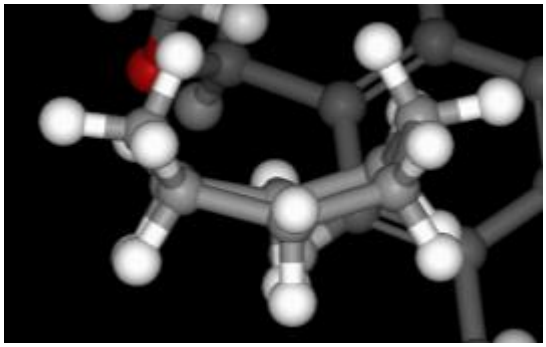
Cyclooctane can be found in several different conformations as components of crystal structures in the CSD. For example, CSD entry WUQVOU contains a cyclooctane molecule in the chair-boat conformation, whereas LULGIK displays a boat-boat conformation. (see below)





Left: the cyclooctane molecule in WUQVOU. Right: the boat-chair conformation of cyclooctane in this structure.





Left: the cyclooctane molecule within LULGIK. Right: the boat-boat conformation of cyclooctane in this structure.

3 Summary

In this module, we have seen that angle strain can occur in cycloalkanes due to deviation from the ideal sp^3 angle of 109.5° and we have also seen that strain can occur when neighbouring bonds are forced to be eclipsed, or partially eclipsed. The strain resulting from eclipsed conformations is called *torsional* strain. We have looked at some specific examples and found that:

- Cyclopropanes are forced to be planar and are highly strained because of both angle strain and the eclipsing of C–H bonds.
- Cyclobutanes adopt a wing-shaped conformation; the deviation from planarity occurs to relieve the eclipsing of neighbouring bonds.
- Cyclopentanes are not planar even though the bond angles in the planar structure would be almost 109.5°. Again, this distortion occurs to relieve eclipsing of adjacent C–H bonds. The minimum energy conformation adopted is therefore a balance between the two opposing types of strain.
- Cyclohexane is strain free because of its puckered chair conformation, in which all bond angles are close to 109.5° and all neighbouring C–H bonds are staggered.
- Rings larger than cyclohexane have greater flexibility and can adopt several different conformations depending on the conditions.

3.1 Next steps

If you would like to study the structures presented in this teaching sheet further, we suggest viewing them in Mercury, where you can customize the view of the molecules and make more advanced measurements. A free-for academic use version of Mercury is available for educational use. To learn more about Mercury, we recommend trying the online module "Visualization 101 – Visualizing Structural Chemistry Data with Mercury". You can find the structures used in this module in the Teaching Subset, which is pre-loaded into Mercury. See the links below for more information.

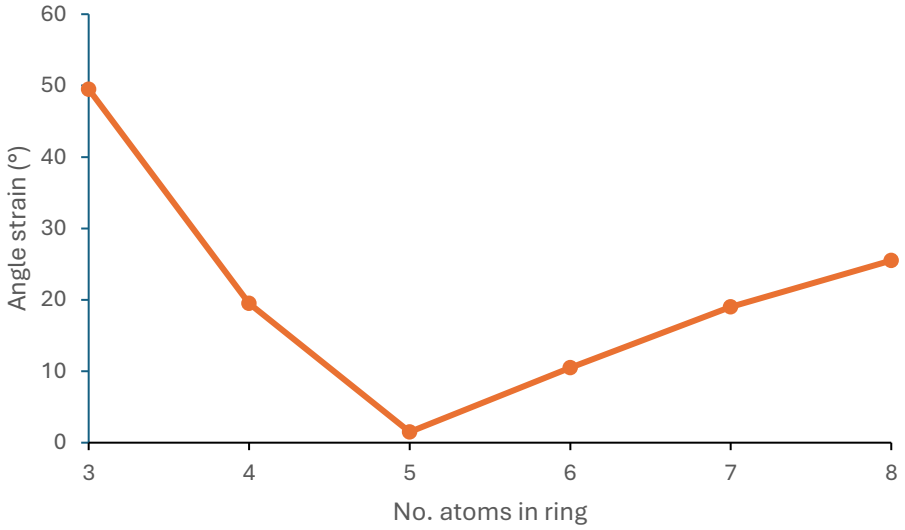
https://www.ccdc.cam.ac.uk/solutions/software/free-mercury/
https://www.ccdc.cam.ac.uk/community/training-and-learning/csdu-modules/visualization-101/
https://www.ccdc.cam.ac.uk/community/education-and-outreach/education/teaching-subset/

If you wish to explore the CSD further and search for structures of interest to you, you can find a number of training resources, including self-guided workshops, online courses and videos to you get started from the CCDC's Training and Learning Web pages.

https://www.ccdc.cam.ac.uk/community/training-and-learning/

4 Answers to exercises

No. atoms in ring	Internal angle in planar structure (°)	Angle strain (°)
3	60	49.5
4	90	19.5
5	108	1.5
6	120	10.5
7	128.5	19.0
8	135	25.5



You should find that the angle strain decreases rapidly from 3 atoms to 5 atoms and then increases, at a slower rate, thereafter.

Refcode	**Internal C–C–C angles (°)**	**Average internal C–C–C angle (°)**
BAVLOZ (using ring with atoms C1-C3-C7-C4-C10-C8)	Angle 1: 108.6	111.1
	Angle 2: 109.5	
	Angle 3: 111.8	
	Angle 4: 112.5	
	Angle 5: 112.7	
	Angle 6: 113.3	
CAFROR	Angle 1: 108.8	110.2
	Angle 2: 109.5	
	Angle 3: 109.9	
	Angle 4: 110.1	
	Angle 5: 111.4	
	Angle 6: 111.6	
CCXAPT (using ring C1-C2-C3-C4-C5-C6)	Angle 1: 105.7	109.9
	Angle 2: 107.2	
	Angle 3: 107.8	
	Angle 4: 111.6	
	Angle 5: 112.5	
	Angle 6: 114.64	
CLCHTF (using ring C1-C2-C3-C4-C5-C6)	Angle 1: 108	109.8
	Angle 2: 109	
	Angle 3: 109	
	Angle 4: 110	
	Angle 5: 111	
	Angle 6: 112	

Refcode	Internal C-C-C Angles	Average Internal C-C-C Angle
CYCHEX	Angle 1: 110.4	111.3
	Angle 2: 110.4	
	Angle 3: 111.3	
	Angle 4: 111.3	
	Angle 5: 112.4	
	Angle 6:112.4	
Average internal C-C-C angle over whole set:		110.5

The strain angle for cyclohexane is therefore 1°.

No. atoms in ring	Strain angle (°)	
	Predicted (in planar rings)	Calculated (crystal structure data)
3	49.5	49.5
4	19.5	21
5	1.5	6
6	10.5	**1**
7	19	6.5
8	25.5	7