L. W. Haynes and his Senior Independent Study students conducted the 2 + 2 photo addition of sulfolene and maleic anhydride. The supposed product is shown below. Haynes crystallized the product of the reaction from acetone and wanted to determine its stereochemistry.

V. B. Pett conducted the X-ray diffraction study while she was on research leave at the Naval Research Laboratory in Washington, D.C. The unit cell has the lattice constants shown in Table 1. To what crystal system does the crystal belong? Include this information in your laboratory report. The actual structure turned out to be the dicarboxylic acid, not the dihydride. Apparently the anhydride opened to the dicarboxylic acid while it was in storage or when it was recrystallized from acetone.

Table 1. Lattice constants for 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide.
The chemical formula is C₈H₁₀O₆S and the formula weight is 234.22 g mol⁻¹. The crystal size was 0.36 x 0.11 x 0.05 mm. The 4458 independent diffraction data were collected on an area detector to a maximum angle of 57.0° at 103 K with molybdenum radiation (λ = 0.71073 Å). The final residual error (R1) is 0.052.¹

\[
\begin{align*}
a &= 18.497 (3) \text{ Å} & \alpha &= 90^\circ. \\
b &= 6.1203 (8) \text{ Å} & \beta &= 112.051 (2)^\circ \\
c &= 17.188 (2) \text{ Å} & \gamma &= 90^\circ. \\
\text{Volume} &= 1803.4 (4) \text{ Å}^3 \\
Z &= 8 \text{ molecules in the unit cell}
\end{align*}
\]

The symmetry of the structure is \(P2_1/c\). From the symbol \(P\) you can see that the unit cell is \textit{primitive}. A primitive unit cell is not \textit{centered}—there are lattice points at the vertices of the unit cell only. A \textit{body-centered} unit cell has identical lattice points at the center of the unit cell; a \textit{face-centered} unit cell has identical lattice points at the center of one or more faces of the unit cell.

There are four symmetry operations including the identity (\(x, y, z\)). One of the symmetry operations is the \textit{inversion} operator \(x, y, z\) so the crystal is \textit{centrosymmetric}. The inversion center is an imaginary point located at the center of the unit cell.

The minimum structure required to generate the entire crystal structure by symmetry is called the \textit{asymmetric unit}. Two molecules with slightly different conformations are included in the asymmetric unit of this structure. Because there are four symmetry operations, there are four asymmetric units in the entire unit cell, or eight molecules. Using the formula weight of the compound and the volume of the unit cell in Table I, calculate the density of the crystal. Include this calculation in your laboratory report. Calculate the maximum resolution of the diffraction obtained for this crystal using Bragg’s Law and include this calculation in your laboratory report.

![ORTEP diagram](image)

Figure 1. ORTEP diagram of the crystal structure of 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide. The ellipsoids are plotted at 50% probability. There are two molecules in the asymmetric
unit. The thermal ellipsoids are relatively small because the diffraction data were obtained at low temperature.

**CrystalMaker investigation of *real space***.

*Real space* is the atoms and molecules that make up the structure of the solid crystal. Using Microsoft Word, open the text version of the cif file and see what information the X-ray diffraction experiment provides about real space. Notice that we have a triple of numbers for each atom; these are the fractional coordinates \((x, y, z)\) for the position of each atom.

In this experiment you will sample distances and angles of covalent bonds and compare these experimental measurements with the idealized geometry you learned in organic chemistry. You will also investigate intermolecular interactions in the crystal.

Double clicking on the cif file provided to you for this laboratory investigation will open the application CrystalMaker. (Or, you can import the text file into CrystalMaker.) You will see a packing diagram of the unit cell. (Model: Show Unit Cell) That is, you will see the contents of the unit cell showing not only the asymmetric unit but also the other molecules generated by symmetry. Because some of the molecules extend outside the boundaries of one unit cell, you see fragments of molecules and isolated atoms. There are a total of eight complete molecules in the display, plus parts of molecules. Notice that there is no atom at the origin of the unit cell. The vertices of the unit cell must be located at identical lattice positions, but these identical lattice positions do not need to coincide with atomic positions.

Besides the structure display window, you will also see other windows: Toolbar, Notes, Atom Info, Output. The **Toolbar** is especially important. The default tool is the Rotate tool (hand). Below it is the move tool; further down are the Auto Scale and Auto Center tools. Investigate the use of the magnify tool by clicking on the magnifying glass and then on the molecule you want to view. Find the Full Screen tool and enlarge the display. You can use the Zapper tool (lightning bolt) to remove atoms from the display. Also test the Zoom in and Zoom out tools (mountains). You probably don't need the Notes window (Window: Hide Notes).
Can you identify two molecules that are related to each other by the inversion center? (Recall that the inversion center is an imaginary point at the center of the unit cell.) Rotate the structure (hand tool). The large mountain icon in the tool palette enables you to zoom in to the center of the unit cell.

To see only the two whole molecules in the asymmetric unit, do the following. First save the file as asymmetric_unit.cif. Then Edit: Structure, Options button. Remove Equivalent Positions 2-4, leaving only the identity operator (x,y,z). Click OK, OK. You will see the two complete molecules in the asymmetric unit, and fragments of other molecules in the unit cell. Next Transform: Set Range. Type the following into the boxes: x goes from −0.1 to 0.9; y goes from -0.205 to 0.75; z goes from −0.154 to 0.9. The latter operation should remove the fragments of other symmetry-related molecules from the display.

Using the Toolbar on the left side of the desktop explore the distance and angle measurements in the structure. Measure distances with the Bond Distance Tool (not the same as the Distance Tool). If you wish, you may work with a partner on this part of the experiment. Construct tables in your notebook or in a Word document to record the important data and include these tables in your laboratory report. It's helpful to display the Output window where the atom names and distances are displayed (Window: Palettes, Output). Then you can copy the important information from the Output window directly into the table in your Word document. You can turn atom labels on and off using the Atom Info window. (Window: Palettes, Atom Info).
Comment on the following aspects of the molecular structure in your laboratory report:

- Measure some representative C–C covalent bond distances. Are the single bond distances the same in the cyclobutane ring and the cyclopentane ring? Measure the C–C bond to the exocyclic C atom.
- What is the C–S covalent bond distance? Why is it longer than the C–C distances?
- What is the O–H covalent bond distance? Why is it shorter than the C–C distance?
- Measure the C–O covalent bond distances; explain why they are different from each other.

Measure angles with the Bond Angle Tool (not the same as the Angle Tool). If you wish, you may work with a partner on this part of the experiment. Construct tables in your notebook to record the data and include these tables in your laboratory report. Comment on the following aspects of the molecular structure in your laboratory report:

- Measure some representative C–C–C angles. (A planar four-membered ring would have 90° angles and a planar five-membered ring would have 108° angles.)
- What are the angles in the carboxyl group? Are these angles typical?
- What are the dihedral (torsion) angles (C–C–C–C) between the C atoms in the four-membered ring? Contrast these angles with those you would expect for a "straight-chain" hydrocarbon. (Review Newman diagrams.)
- Five-membered rings exhibit two conformational types: twist (C₂ point symmetry) or envelope (C₅ point symmetry). What symmetry do you see in the five-membered rings of the two molecules in this structure?
- Why are there two molecules in the asymmetric unit? One might think that one molecule plus symmetry operations would be sufficient to describe the entire solid-state structure. Hint: how are the two molecules different from each other?

There are several hydrogen bonding interactions in this crystal structure. Be sure you understand what a hydrogen bond is before you begin this work! Look for hydrogen bonds in the asymmetric unit by measuring distances between likely atoms. The distance between a hydrogen atom and the acceptor atom in a typical hydrogen bond is about 2 Å. The angle D–H······A is
usually 160-180°. Use the Info tool (in the toolbar) to find out the names of the atoms that participate in hydrogen bonding. Construct a table of hydrogen bond data in your notebook or Word document, with the names of the atoms and the distance and angle information.

We can use the packing diagram to discover more intermolecular interactions between molecules. Close the file you were working with and open the cif file provided to you by the instructor. The Magnify tool is helpful in this work. Click on the magnifying glass in the Tool bar, and then click on an atom to expand parts of the structure where you expect to see hydrogen bonding.

This small-molecule structure is high enough resolution to include hydrogen atoms. In a protein structure, individual coordinates for hydrogen atoms are not typically found. However, we can deduce that there are hydrogen bonds between appropriate donor (D) and acceptor (A) atoms if the distance between them is about 3 Å. For the hydrogen bonds that you found in this structure, verify that the donor-acceptor distance is about 3 Å. If you find any other non-bonded interatomic distances that are about 3 Å, how do you interpret these interactions?

**SingleCrystal investigation of reciprocal space.**

*Reciprocal space* is the experimental diffraction pattern. The goal here is for you to discover a relationship between atomic positions and intensity of spots in the diffraction pattern.

- Launch SingleCrystal.
- In CrystalMaker, open the cif file provided to you by the instructor. (The file that contains the asymmetric unit cannot be used for this part of the experiment because it doesn’t include all the symmetry operations.) Then Transform: Diffraction Pattern: Single Crystal.
- In SingleCrystal, Diffract: Weighted Reciprocal Lattice
  View: Show Labels
  View: Show Forbidden Reflections (these will be represented as the tiniest dot)
- Use the pull-down menu at bottom left to select direction to view diffraction pattern (If you cannot see the tools at the bottom of the window, click on the *hkl* icon at top.)
- Set Intensity saturation pull-down menu at bottom to 50 or 10.
• Use Magnify tool at top to expand the pattern so you can read the $hkl$ values easily.

Select direction at bottom left to [1 0 0]. You are looking at the zero level of the diffraction pattern—the $hkl$ values for every diffraction spot has $h=0$. You see the $b^*$ and $c^*$ axes at right angles to each other. The asterisk after the axis symbol reminds you that these are axes in reciprocal space. The axes cross at the origin, the position of the direct beam, with $hkl$ 000. Print the diffraction pattern and mark the axes on the pattern.

**Systematically absent** reflections result when the diffracted waves from two symmetry-related atoms cancel out. Use the Select Tool (top of window) to click on the various reflections to read the intensity ($I/I_{\text{max}}$). Look for a regular pattern of absences that could be summarized as a general rule that could be expressed mathematically. (For example, for face-centered crystals, the Miller indices are either all even or all odd for observed reflections. Another example is that for some symmetry elements, the $(00l)$ reflections with odd $l$ along the $c^*$ axis are absent.) Circle the reflection spots on your printout that are systematically (not randomly) absent.

Now set the view direction [001], print out the diffraction pattern, and mark the axes on the pattern. Do you see a pattern of systematic absences? Circle the reflection spots that are systematically (not randomly) absent.

Select direction [0 1 0] to see the $a^*c^*$ plane. What systematic absences do you see on this zero level? Mark the axes and the systematic absences on the printout.

Figure out how to measure the length of the $b$ axis in real space from the diffraction pattern. Compare the measurement from the diffraction pattern to the length of the $b$ axis in Table 1. Figure out how to measure the $\beta$ angle between axes $a$ and $c$ in real space from the diffraction pattern. Compare the measurement to the value in Table 1.

Notice that the spots have very different intensities. It's the intensity information that ultimately gives us the information on where the atoms are in the unit cell. Find a particularly intense spot in the diffraction pattern. Go back to the real space representation of the structure, choose
Transform: Lattice Plane. Type the \((hkl)\) values for the intense diffraction spot into the boxes, and check the box Show Lattice Plane. Can you rationalize why this particular set of planes diffracts X rays very strongly compared to the other planes? Answer this question in your laboratory report.

Using the arrow tool, click on a range of spots to look at the \(d\) spacing. Where in the photograph are the high-resolution data? Where in the photograph are the low-resolution data? Now try to make a generalization about the intensity of the data and the resolution. Which data must we have to know the structure precisely? Why would intense radiation at the synchrotron be helpful? Answer these questions in your laboratory report.

Finally, select View: Colour by Phase. Good grief! If we had only used color X-ray film, we could have solved the phase problem easily! (Just kidding.) Actually, the only reason we can assign a phase to each spot in diffraction space is that we now know where the atoms are in real space. We can calculate the structure factors sums and find out whether the sums are positive or negative. In order to know the phases, we need to know where the atoms are—but we can’t calculate an electron density map to find the atoms until we know the phases! This circular dilemma is the essence of the phase problem.

**Laboratory report**

Your laboratory report should be a journal of discovery. Include calculations, tables of values, and answers to the questions in this laboratory handout, in essay form. You may divide this material into Introduction, Experimental, Results, and Discussion if you wish. Or, you may feel that there are other logical ways to divide up the information and insights that you gained from your analysis of the crystal structure.
Helpful info on SingleCrystal

The measurements along the a* and c* axes don't give the lattice constants of the unit cell, because the angle between these axes is not 90°.

The wavelength and scale don't seem to do anything with weighted reciprocal lattice. The diffraction pattern looks the same and the measurements are the same too so it doesn't seem to matter how they are set.