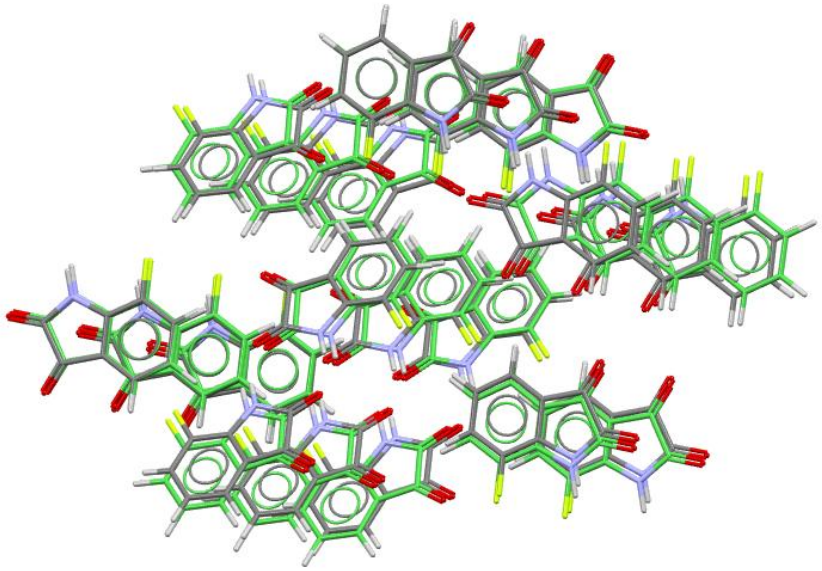
Crystal Structure Optimisation in Mercury

Developed using 2026.1 CSD release



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Introduction

This workshop will focus on Crystal Optimiser, which is part of the CSD-Materials suite. Crystal Optimiser make use of *force field*-based calculations to provide information that may be useful for understanding energetics in crystal structures.

Structure optimisation is often performed prior to undertaking further calculations. One application in the context of the CSD is to derive a single consistent structure model from several independent reports of the same crystal structure, possibly under different conditions, or to help with poor quality or partially complete structures. Crystal Optimiser seeks to optimise the geometry of a crystal structure to achieve the lowest *lattice energy* by using a chosen force field to evaluate intermolecular interaction energies. Intramolecular geometry optimisation is also available independently *via* the Molecule Optimiser, however we will not cover this in this workshop.

Learning Outcomes

At the end of this workshop, you will be able to:

- Use the Crystal Optimiser tool in Mercury to calculate the optimised structures of some polymorphs
- Evaluate the similarity of experimental and optimised crystal structures using the Crystal Packing Similarity tool in Mercury

This workshop will take approximately **25 minutes** to be completed. The words in *Blue Italic* in the text are linked and reported in the Glossary at the end of this handout.

Prerequisite Skills

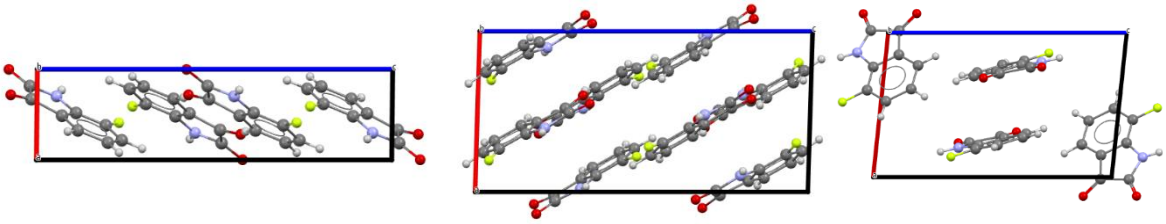
Familiarity with the Mercury interface is desirable but not essential. You may find the free course https://www.ccdc.cam.ac.uk/community/training-and-learning/csdu-modules/visualization-101/ helpful if you are not already familiar with Mercury.

Materials

Please download the workshop folder here. It contains CIF files of DFT-optimised crystal structures that are required.

Example: Optimising Crystal Structures in Mercury

In this section, we will optimise the structures of three *polymorphs* of 7-fluoroisatin (CSD refcodes NIZVAU-NIZVAU02) using Crystal Optimiser. We will compare both the *CLP* force field-optimised and *DFT*-optimised structures with the experimental ones using a Crystal Packing Similarity search.

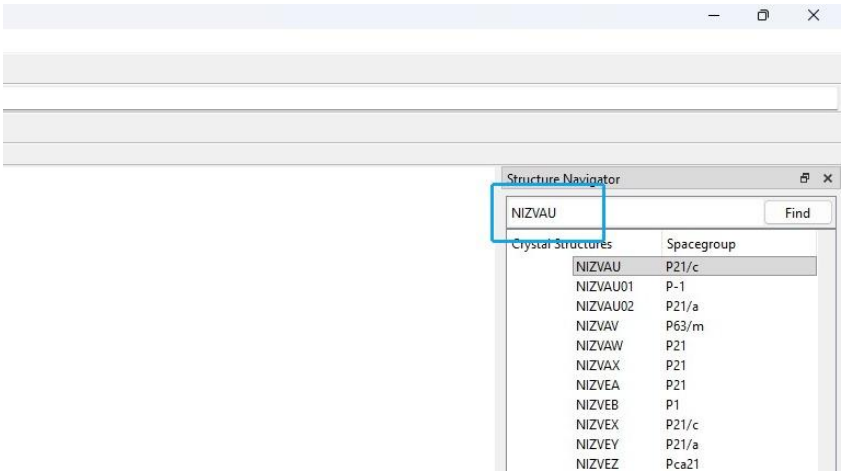


NIZVAU NIZVAU01 NIZVAU02

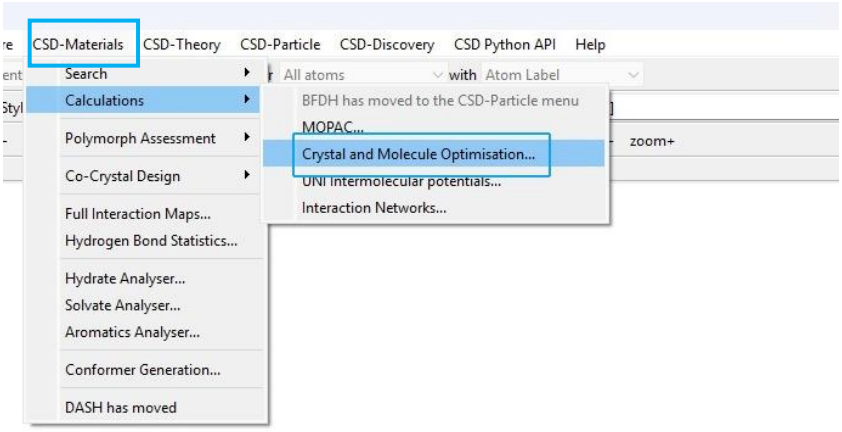
Three polymorphs of 7-fluoroisatin showing different packing and unit cells.

Optimising a Crystal Structure

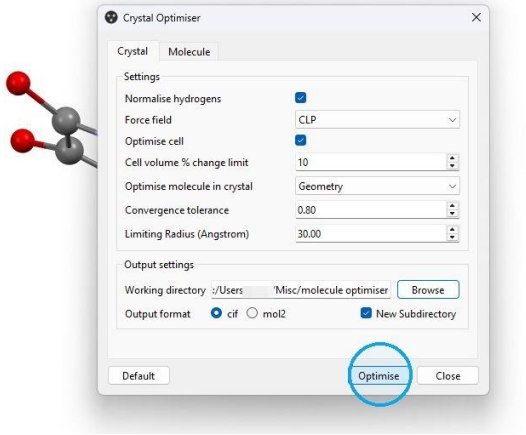
1. In the Structure Navigator, type "NIZVAU".



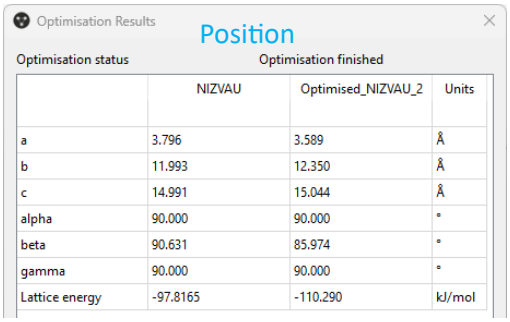
2. From the **CSD-Materials** menu, select **Calculations > Crystal and Molecule Optimisation**.



3. In the Crystal Optimiser tab, make sure that the **Default** settings are selected. Choose a working directory and then click **Optimise**.



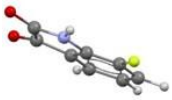
Tip: There are several force fields available to choose from including CLP, Dreiding II, Momany, Gavezzotti and CSD-OPCS16. You may need to experiment to find the best one for your purposes.

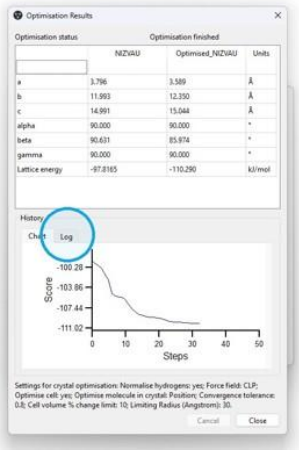


	NIZVAU	Optimised_NIZVAU_2	Units
a	3.796	3.589	Å
b	11.993	12.350	Å
c	14.991	15.044	Å
alpha	90.000	90.000	°
beta	90.631	85.974	°
gamma	90.000	90.000	°
Lattice energy	-97.8165	-110.290	kJ/mol

The options in *Optimise molecule in crystal* are "Position", which only optimises molecule position, not geometry, and "Geometry", which optimises both position and molecular geometry. 7-Fluoroisatin is a rigid molecule, so it makes little difference in this case.

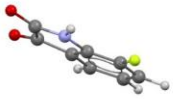
4. The calculation will run and the cell parameters and lattice energy will be updated with each step. A trace of the lattice energy is also displayed in the History area. For further details, click on the Log tab.

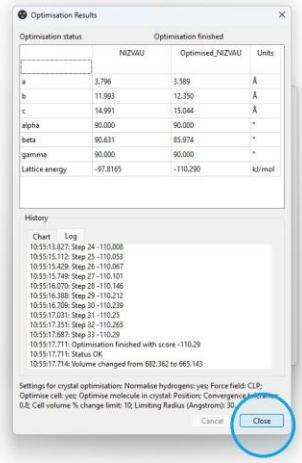




Tip: The *Convergence tolerance* controls the degree of change in energy or score that is acceptable before a structure is considered optimised. A higher value will typically give a faster optimisation, a lower value will typically give a more optimised structure.

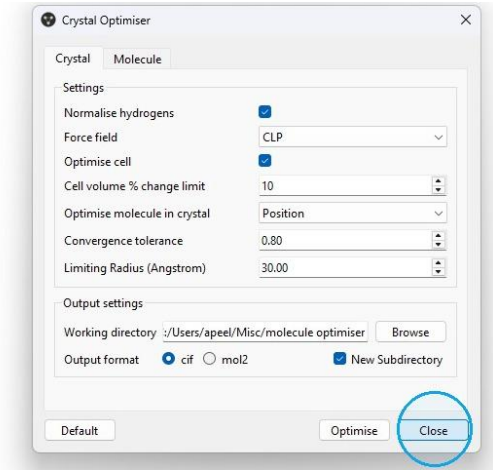
5. Inspect the changes to the parameters that have been made. When you are ready, click **Close** in the Optimisation Results window.



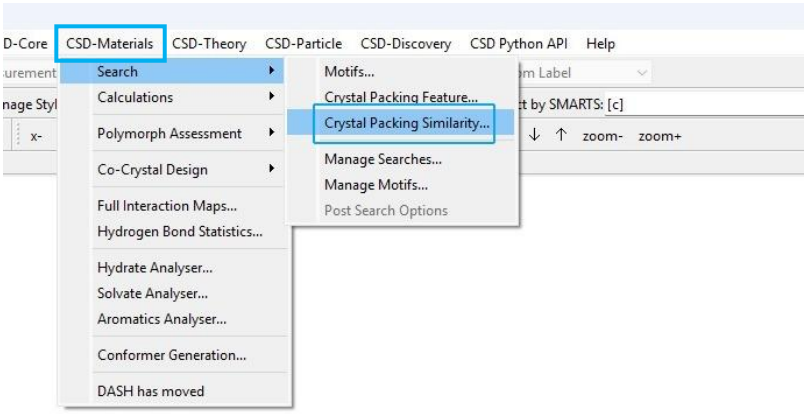


Tip: A CIF or MOL2 file (depending on your choice in the setup) will have been written to the directory selected in step 3 so you can view the optimised structure/inspect the parameters at a later time too.

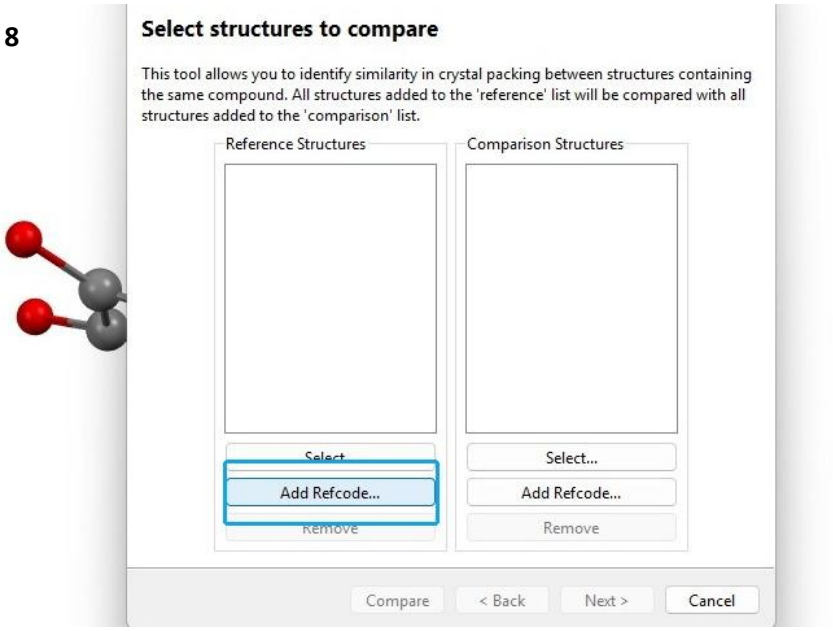
6. Click **Close** in the Crystal Optimiser dialog.



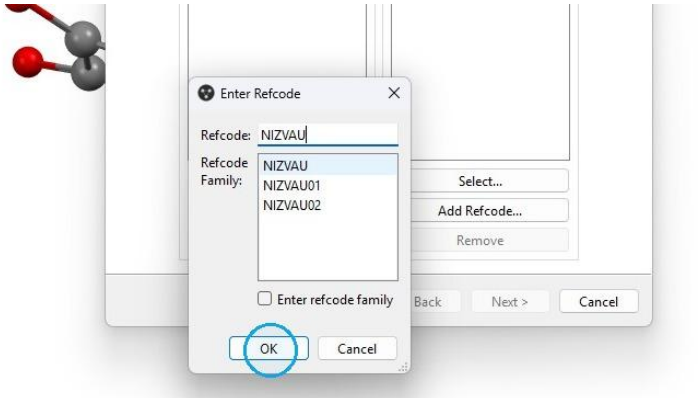
7. To compare the optimised structure and the one from DFT calculations (click here for details) with the experimental structure, we will use the Crystal Packing Similarity tool. This will help us understand how much the crystal structure changed as a result of geometry optimisation in each case. From the **CSD-Materials** Menu, select **Search > Crystal Packing Similarity**.



8. The Crystal Packing Similarity Wizard will open. Click **Add Refcode** in the Reference Structures section if you have the full CSD installed.

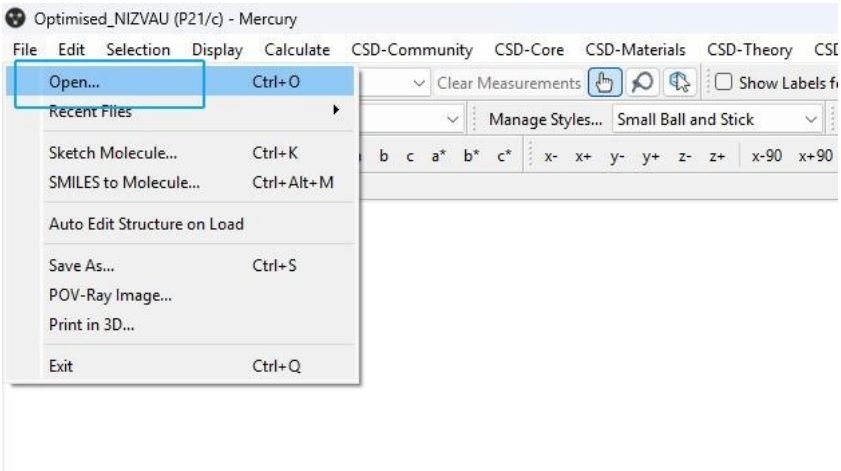


9. Enter the “NIZVAU” refcode, then click **OK**.



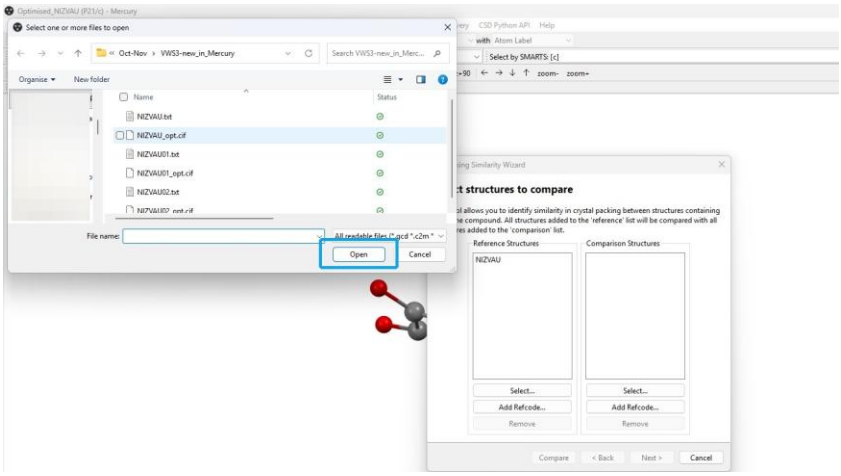
Tip: The dialogue automatically detects other structures in the refcode family which can all be selected by ticking **Enter refcode family**. In this example, we want a single reference structure, so leave this **unticked**.

10. We will now open the CIF of a DFT-optimised structure of NIZVAU. From the **File** menu, select **Open**.



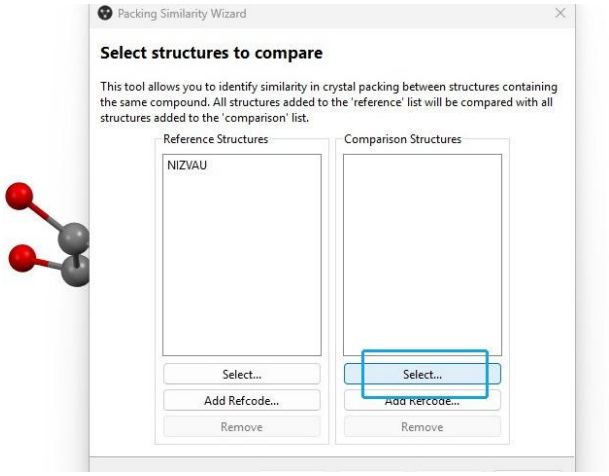
Important! If you have not already downloaded and unpacked the DFT optimised structure files, please download them from here now.

11. Navigate to the location you saved the workshop files, select “NIZVAU_opt.cif” and click **Open**.

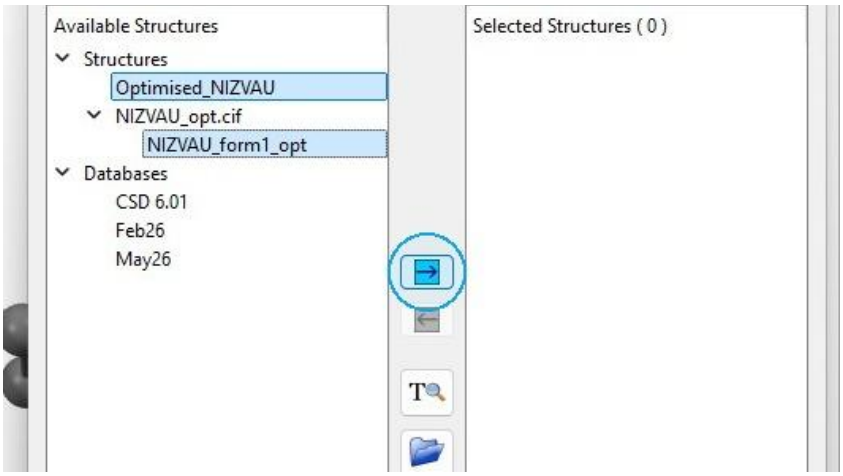


Tip: Opening the file in Mercury makes it available to select during step 13. If you prefer you can do this directly in step 13 and skip this step.

12. Click **Select** in the Comparison Structures section.

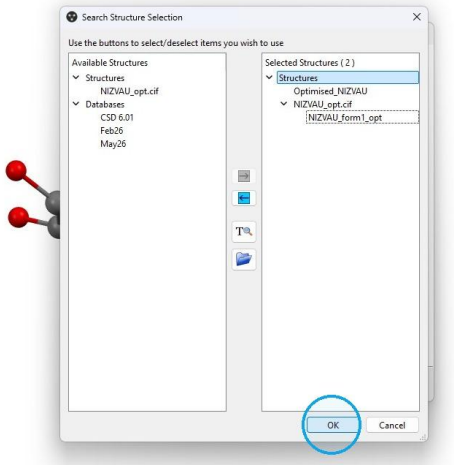


13. Select "Optimised_NIZVAU", hold down Ctrl and click on “NIZVAU_form_1_opt”, then click the blue arrow to move the structures to the Selected Structures.

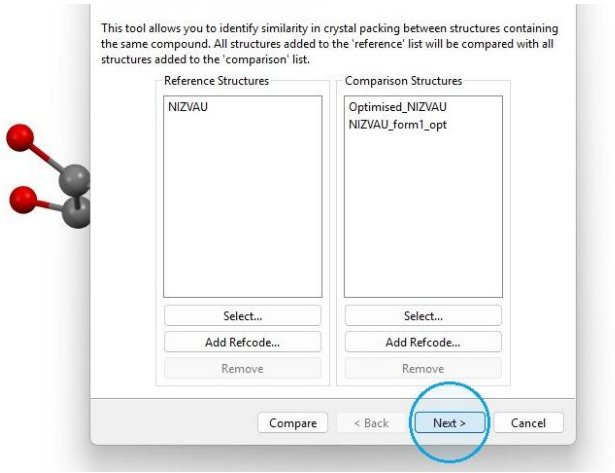


Tip: If you prefer to skip opening the DFT-optimised file from the File menu in Mercury, you can use the folder icon here to select it. You will still need to move the forcefield optimised structure from the previous calculation to the Selected Structures panel as shown.

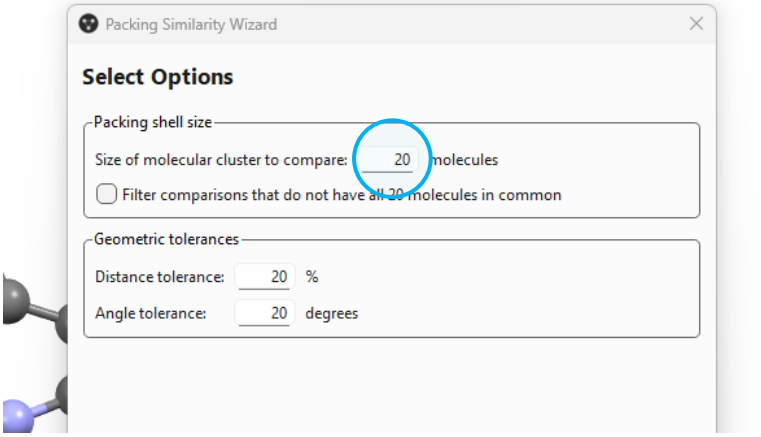
14. Click **OK**.



15. Click **Next**.

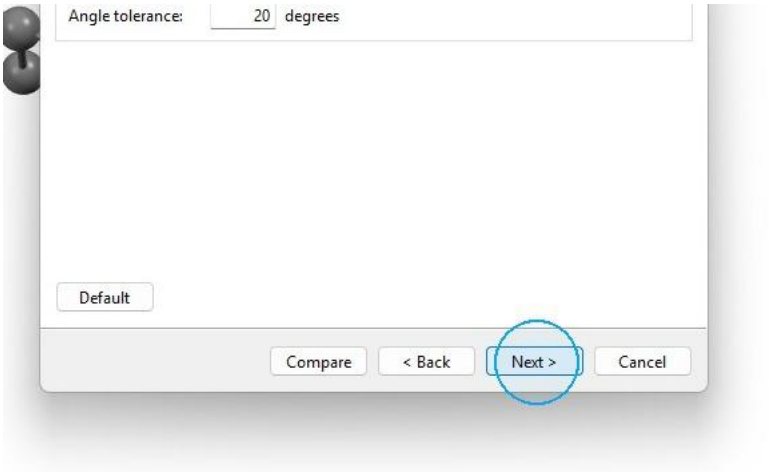


16. Set the packing shell size to 20 molecules. Leave the other settings as their default values.

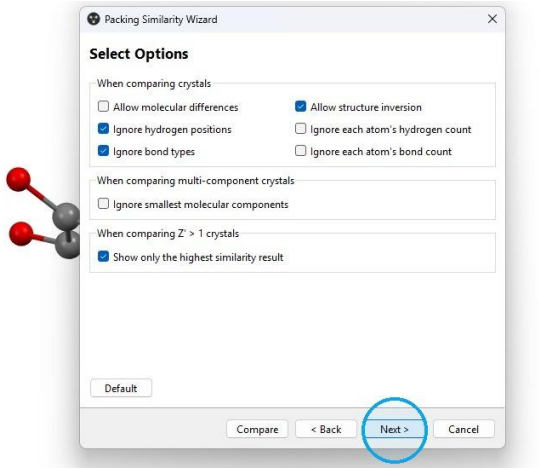


Info: the cluster of *n* molecules is composed of a central reference molecule plus *n*−1 surrounding molecules.

17. Click **Next**.

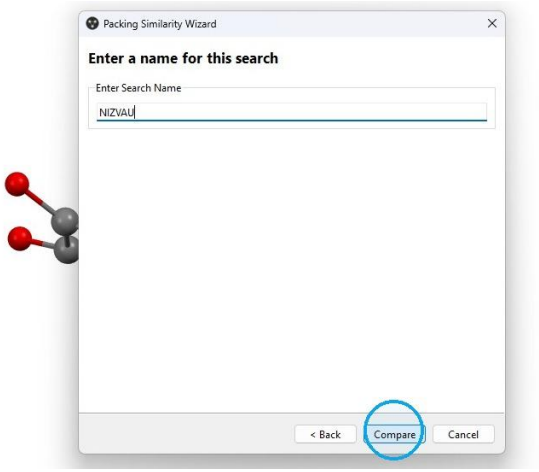


18. In the next section of the wizard, you will see some further settings. Leave the settings as their default values and click **Next**.

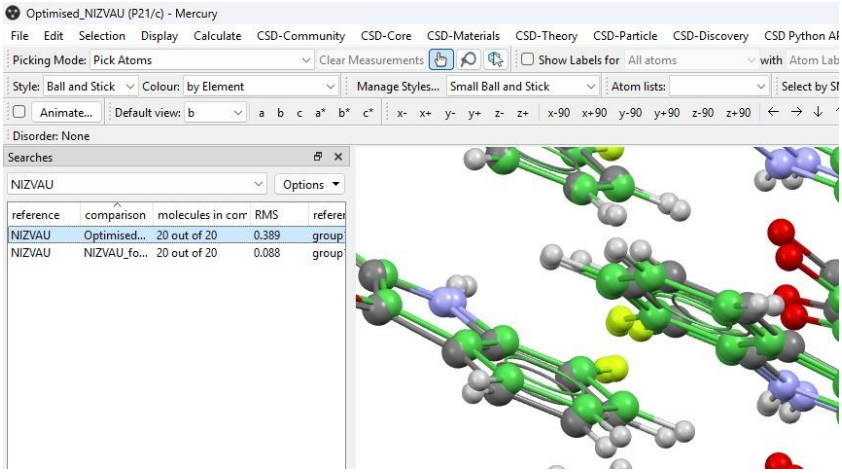


Tip: for a detailed explanation of the search options available, see the Mercury user guide.

19. Give the search a suitable name, then click **Compare**.

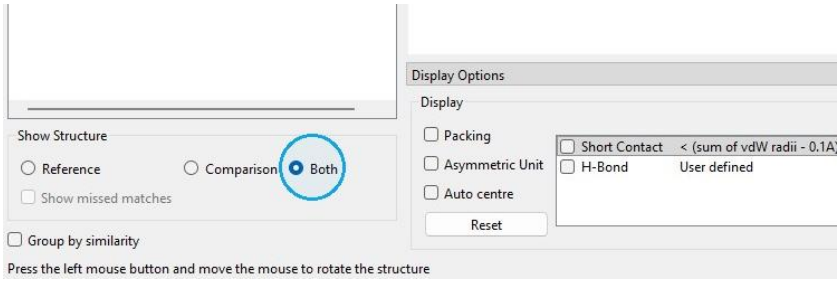


20. When the calculation has run, you will see a summary of the results in the Searches panel. You will see that in both cases it was possible to overlay 20 out of 20 molecules in the cluster, with relatively low RMS.

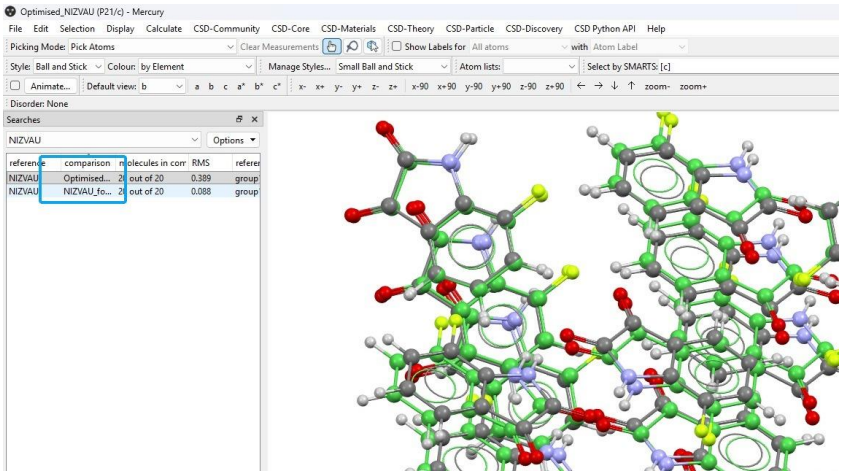


Tip: The RMS deviation of the overlay is calculated from the distances between the matched atoms in each molecular cluster.

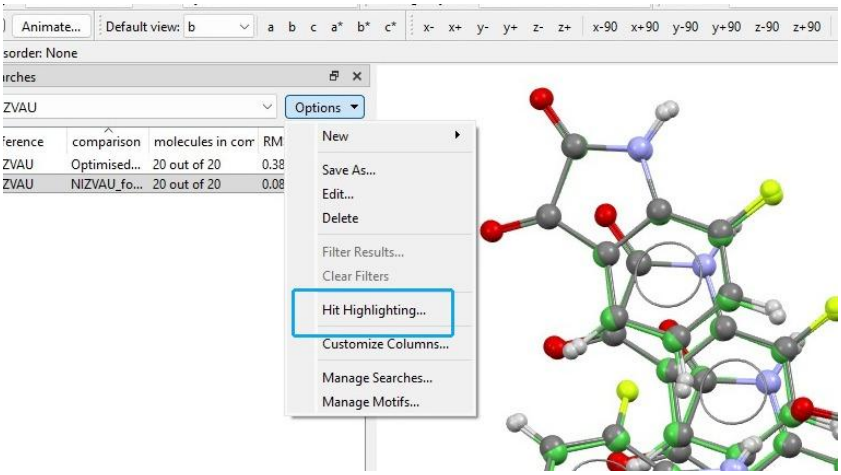
21. To make sure that you can see both the experimental structure and the optimized structure (whichever is selected in the Searches panel), click the **Both** radio button at the bottom of the panel.



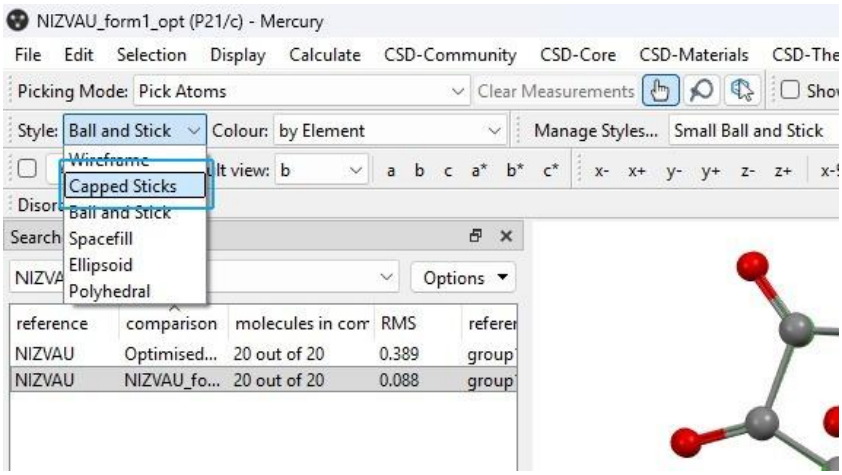
22. Click on a row in in the search results to display the overlay in the visualiser.



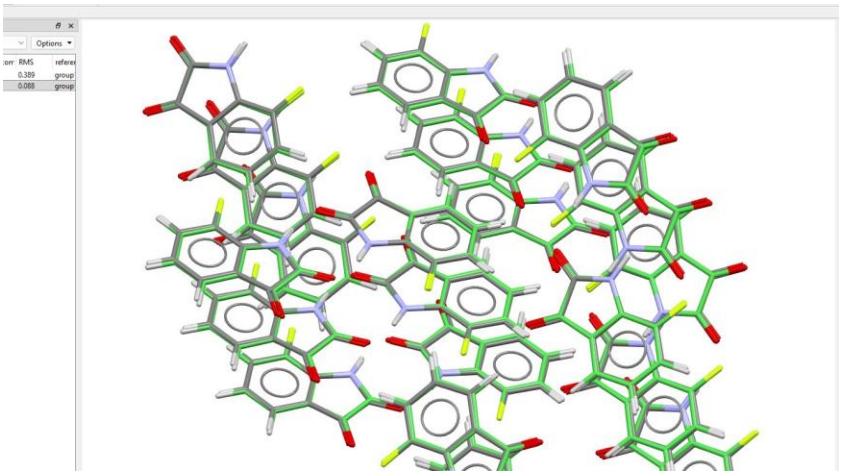
23. If you wish to customise the way that the reference and comparison structures are displayed, you can do this from the **Options > Hit Highlighting** menu option.



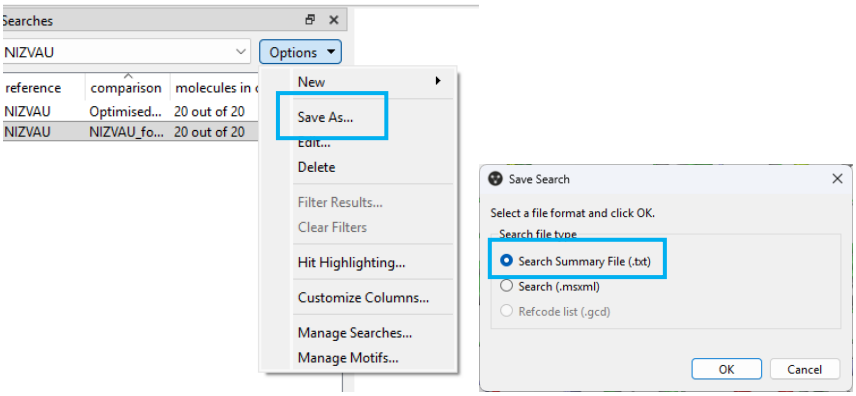
24. To quickly change the style of the whole view, you can select from the **Style** drop-down menu. You might find a style such as capped sticks or wireframe easier to look at.



25. Take a moment to inspect the overlay in the Mercury visualiser. You can see that visually the overlay is very good.



26. If you wish to save a summary of the packing similarity search, you can do this by going to **Options > Save As**. A search summary file is sufficient for our purposes.



Extension

27. In the workshop materials, you will find the DFT-optimised structures for Forms II and III of 7-fluoroisatin, which correspond to NIZVAU01 and NIZVAU02 in the CSD. Repeat the crystal structure optimisation of the CSD structures using Crystal Optimiser and compare the resulting optimised structures and corresponding DFT-optimised ones to the CSD structures using the Crystal Packing Similarity tool. How do the results compare with those in this example? Record your results (you may wish to use a table like the one shown below).

Refcode	**Lattice energy / kJ mol^{-1}**	**Crystal Optimiser *vs* CSD entry**		**DFT vs CSD entry**	
		Matched molecules / 20	**RMS**	**Matched molecules / 20**	**RMS**
NIZVAU	−110.290	20	0.389	20	0.088
NIZVAU01					
NIZVAU02					

* If you have used 'Geometry' optimisation, you will get a 'score' rather than a lattice energy.

You might also like to try comparing the results using different forcefields. Is the energy rank of the different polymorphs the same? Please note that the Momany force field does not include parameters for fluorine and cannot be used in this case. Run time may vary between force fields.

Click here to see the answers.

Details of DFT Optimisation

The crystal structures of 7-fluoroisatin were optimised with the VASP program, using PAW pseudopotentials and the Tkatchenko-Scheffler dispersion correction.

Conclusions

In this exercise we have used Crystal Optimiser to optimise crystal structures according to a chosen force field. The calculations were quick and the resulting structures do not deviate greatly from the input. DFT optimisation returns structures that are closer to the input ones, hence whilst both methods are useful, for very accurate studies, the DFT calculations would still be preferable in this case (though more computationally expensive).

Summary

In this workshop we have demonstrated the Crystal Optimiser in Mercury. You should now be able to:

- Use the Crystal Optimiser to optimise a crystal structure according to a chosen force field
- Compare an optimised structure with a reference structure using Crystal Packing Similarity tool

For your reference, you can find the user manual here https://www.ccdc.cam.ac.uk/media/mercury-1.pdf.

Next Steps

If you have found the tools shown in this workshop useful, you might like to try some of our other self-guided workshops from the CSD-Materials and CSD-Particle areas, where you can explore other tools to study intermolecular interactions and morphology.

https://www.ccdc.cam.ac.uk/community/training-and-learning/workshop-materials/csd-materials-workshops/

https://www.ccdc.cam.ac.uk/community/training-and-learning/workshop-materials/csd-particle-workshops/

How to cite these tools

Mercury: C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst.*, **53**, 226–235, 2020 DOI: 10.1107/S1600576719014092

A comparison of the force fields implemented in Crystal Optimiser can be found in this paper: L. M. Hunnisett, P. Sacchi and A. G. P. Maloney, *Struct. Chem.*, 2026, **37**, 1063–1067 DOI: https://doi.org/10.1007/s11224-025-02715-z

Answers to Exercises

Using the CLP force field with Position optimisation

Refcode	Lattice energy/ kJ mol^{-1}	Crystal Optimiser *vs* CSD entry		DFT vs CSD entry	
		Matched molecules / 20	RMS	Matched molecules / 20	RMS
NIZVAU	−110.290	20	0.389	20	0.088
NIZVAU01	−109.291	20	0.264	20	0.088
NIZVAU02	−104.791	20	0.304	20	0.075

You can find the results of using different force fields (and DFT) with the three polymorphs in the table below. Please note that the Momany force field does not contain parameters for fluorine and cannot be used with this molecule.

Refcode	Force field	Matched molecules / 20	RMS	Lattice energy / kJ mol^{-1}
NIZVAU	Dreiding II	20	0.297	-91.71
NIZVAU01	Dreiding II	20	0.261	-90.92
NIZVAU02	Dreiding II	19	0.419	-87.22
NIZVAU	Gavezzotti	20	0.268	-111.53
NIZVAU01	Gavezzotti	20	0.216	-106.97
NIZVAU02	Gavezzotti	10	0.752	-105.44
NIZVAU	CLP	20	0.389	-110.29
NIZVAU01	CLP	20	0.269	-109.30
NIZVAU02	CLP	20	0.316	-105.15
NIZVAU	CSD-OPCS16	20	0.271	-98.16
NIZVAU01	CSD-OPCS16	20	0.279	-93.97
NIZVAU02	CSD-OPCS16	11	0.611	-91.96
NIZVAU	DFT	20	0.088	-118.96
NIZVAU01	DFT	20	0.088	-119.15
NIZVAU02	DFT	20	0.075	-117.68

Glossary

CLP

Coulomb-London-Pauli (CLP) force field. An atom–atom intermolecular force field with subdivision of interaction energies into Coulombic-polarization, dispersion (London) and repulsion (Pauli) terms. See *New J. Chem.* 2011, **35**, 1360–1368 DOI: 10.1039/c0nj00982b for further information.

Density Functional Theory

A quantum-mechanical method that calculates crystal energies from the electron density, enabling accurate structure optimisation and lattice energy calculations.

Disorder

A disorder assembly is a cluster of atoms that show long range positional disorder but are locally ordered. A disorder groups consists of the atoms in the assembly that are linked by occupancy. E.g. an isopropyl group disordered over two sites has one disorder assembly and two disorder groups.

Force field

A parameterised mathematical model used to calculate the potential energy of a crystal structure from atomic positions, enabling estimation of lattice energies and crystal packing interactions. Mathematical descriptions of the force fields implemented in Crystal Optimiser can be found here.

Lattice energy

The lattice energy corresponds to the total stabilisation energy (per molecule) related to the transfer of an isolated gas phase molecule, having no intermolecular interactions, into the crystal, where non-bonded interactions of various nature are set up with surrounding molecules.

Structure optimisation

The process of modifying a crystal structure to minimise the energy calculated by a force field (or other energy model), yielding a stable crystal geometry.

Polymorphs

Polymorphism is the occurrence of two or more crystalline forms of the same substance. Where available, polymorph information can be displayed for Cambridge Structural Database (CSD) structures. Structures known to be polymorphic contain comments which include the word polymorph (when reported by the author), e.g., non-triboluminescent polymorph. There is also a CSD subset of polymorphic structures.

Score

Crystal Optimiser tries to minimize a score, Z_{total}, by optimizing the positions of the molecules in the crystal and/or by optimizing their geometry using a knowledge-based method (KBF).[1] The score is composed of two terms:

$$Z_{total} = Z_{inter}^{FF} + \kappa Z_{intra}^{KBF}$$

If the molecule geometry is kept fixed during optimisation, the final optimiser score will only be composed of the intermolecular term Z_{inter}^{FF}, which accounts for the stabilisation of the crystal structure stemming from intermolecular interactions only. If the molecule geometry is changed, however, the additional term Z_{intra}^{KBF} , scaled by a factor κ, is also added. Since the score Z_{intra}^{KBF} is calculated by comparing molecular geometries with statistical values from the CSD database, its value will not directly represent an energy. Because of this, Z_{total} scores cannot be compared directly to sublimation enthalpies, i.e., they should not be considered as a direct indication of the stability of a crystal structure (in strict thermodynamic terms).

[1] J. C. Cole, C. R. Groom, O. Korb, P. McCabe and G. P. Shields, J. *Chem, Inf., Model*., 2016, **56**, 652–661 DOI: 10.1021/acs.jcim.5b00712

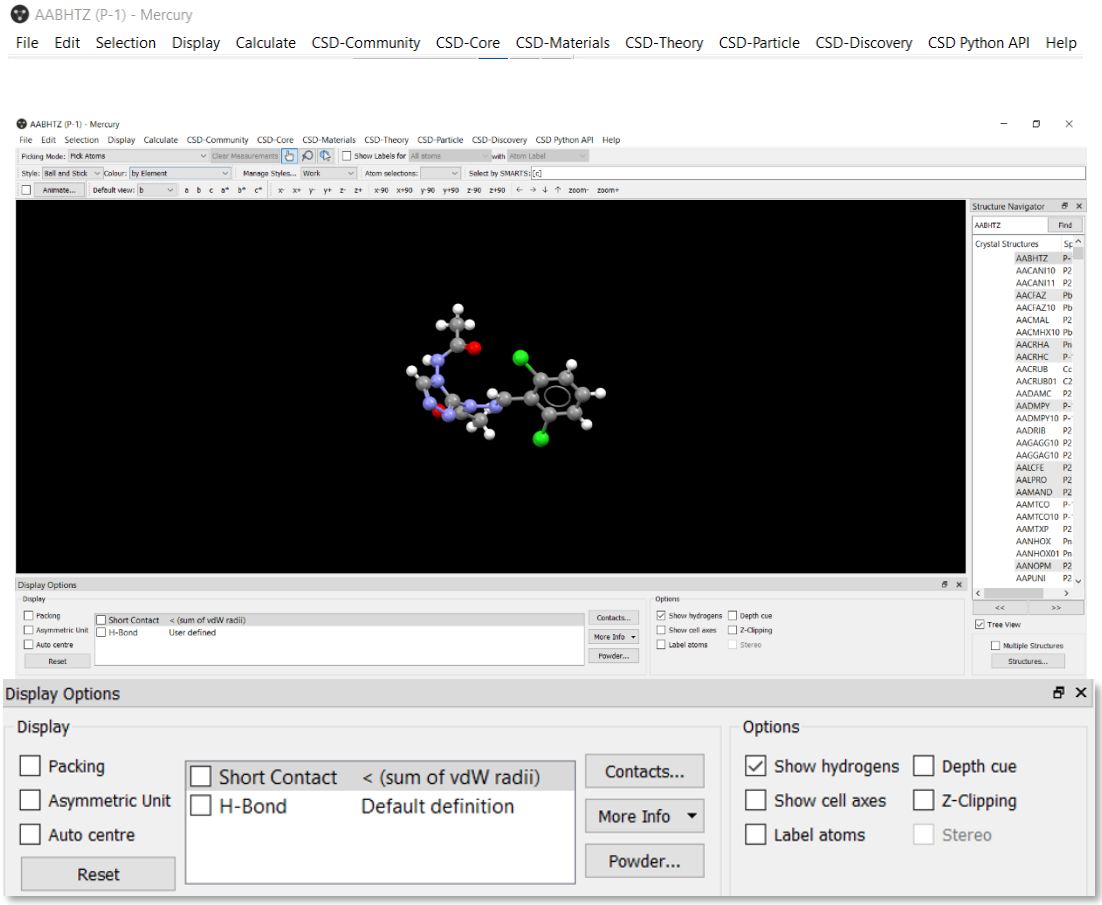
Basics of Mercury Visualization

Mercury is the CCDC's visualization software to view 3D structures of small molecules, generate images, and animations of molecules

In the following we will see some of the basics of navigation and visualization in Mercury that you will find helpful to support your analysis. You can also find an extensive range of video resources here.

In the **Mercury interface** we find:

- **At the top**: list of menus from which we can access visualization and analysis options, and other CSD components such as CSD-Materials.
- **On the right-hand side**: the **Structure Navigator**, with the database loaded (depending on your licence). The Structure Navigator allows you to select a refcode to visualize in the main Mercury window.
- **Beneath the main display window: Display options toolbar.** You can quickly view a packing diagram, display Hydrogen bonding and detailed information about the molecule using the More Info option.



Using the **mouse to enhance visualization**:



- Left mouse button and move – rotate molecules.
- Middle Mouse wheel – move molecules up and down.
- Right mouse button and move up and down – zoom in and out of molecules.
- Shift + Left mouse button and move - rotate in the plane molecules.
- Ctrl + Left mouse button and move - translate molecules.

Additional gestures may be available with trackpads.

Right click:

a) Near a molecule and
b) Away from a molecule

