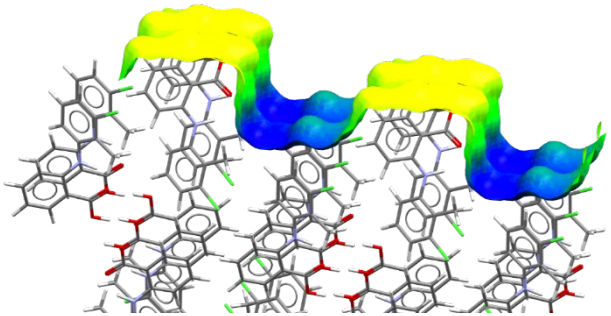
Investigation of Plastic and Elastic Properties with CSD-Particle Tools in Mercury (PAR-002)

Developed using
2022.3 CSD Release



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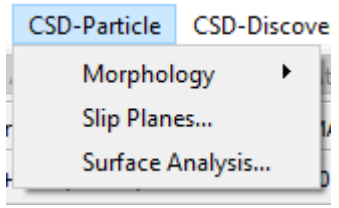
Introduction

This workshop shows you how to use functionality from the CSD-Particle suite to visualize and analyse the mechanical and chemical properties of molecular crystals. It uses quick computational models and algorithms, alongside data from the Cambridge Structural Database (CSD), to provide both qualitative and quantitative analyses of particle shape as well as surface and bulk properties. Such features are found under the CSD-Particle menu in Mercury.



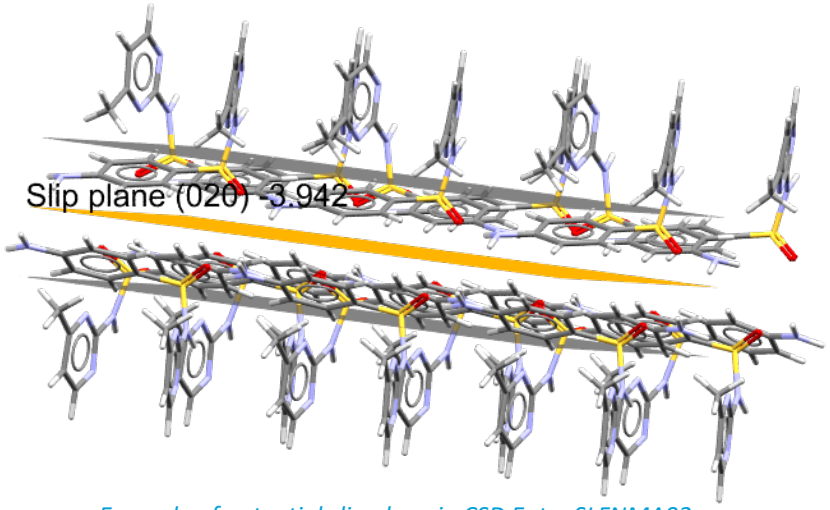
Before beginning this workshop, ensure that you have a registered copy of CSD-Materials or CSD-Enterprise installed on your computer. Please contact your site administrator or workshop host for further information.

Learning Outcomes

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

- Identify and analyse potential slip planes.
- Analyse particle surfaces.

Note: The words in *Blue Italic* in the text are reported in the Glossary at the end of this handout. The exercise in this handout will take approximately ***30 minutes*** to be completed.



Example of potential slip plane in CSD Entry SLFNMA02.

Pre-required Skills

The following exercises assume you have a working knowledge of the basics of visualizing structures with Mercury, namely, how to display and manipulate structures from a 3D coordinates file.

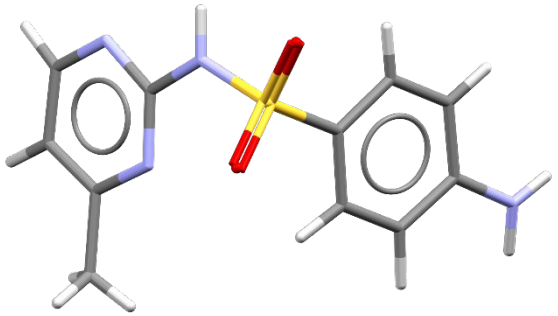
Materials

There are no additional materials required for this workshop.

Example 1. Slip Planes analysis to investigate elastic properties

In this example, we will focus on two polymorphs of sulfamerazine to investigate their different tabletability and properties. Our focus will be on CSD Entries SLFNMA02 and SLFNMA01, displaying plastic and *elastic* behaviours respectively based on experimental data. We will use the *Slip Planes* tools to try and understand where the slip planes might indicate elastic or plastic behaviour.

The Slip Planes tool shows potential slip planes based on the separation of the slabs.



A molecule of 2-p-Aminobenzene-sulfonamido-4-methylpyrimidine from CSD Entry SLFNMA02.

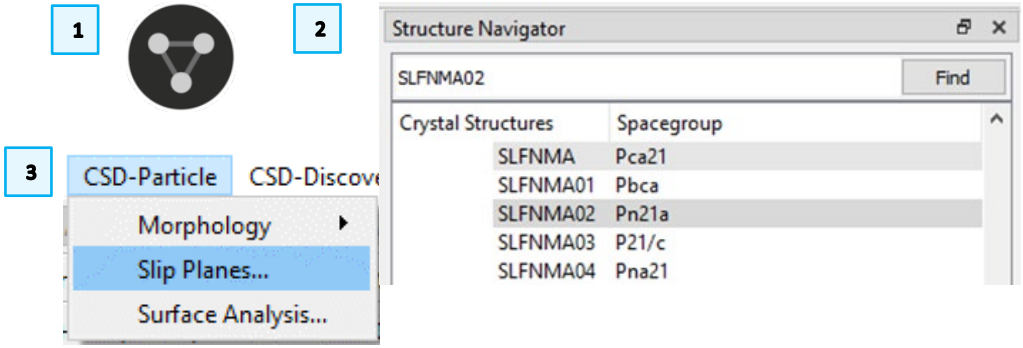
Calculation of potential slip planes

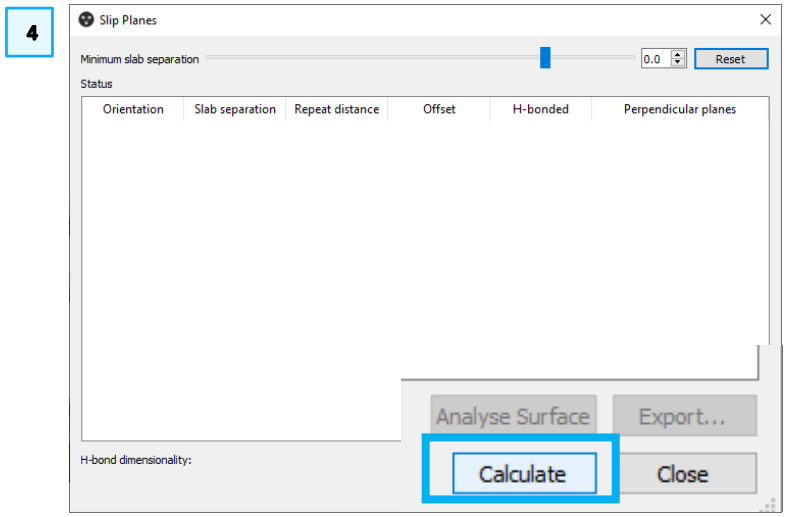
1. Open Mercury by double-clicking the Mercury icon on the desktop.

2. In the *Structure Navigator* on the right-hand side of the Mercury interface type the refcode SLFNMA02 to bring up the first *polymorph* of sulfamerazine that we are going to investigate, i.e. the *plastic* one.

3. From the top-level menu select **CSD-Particle > Slip Planes…** to launch the *Slip Planes* window.

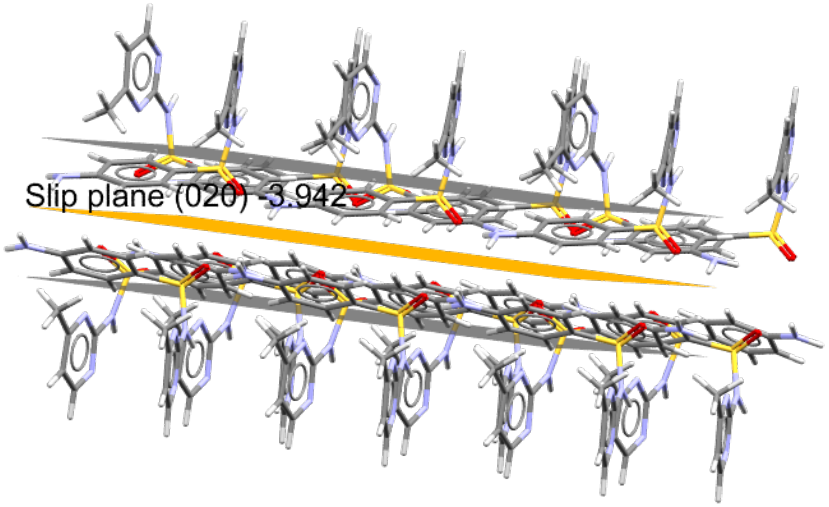
4. Observe that the *minimum slab separation* is set to 0.0 Å. To start the calculation, click **Calculate** at the bottom of the *Slip Planes* window.





5. You will see that the table is now populated with an entry representing a potential slip plane with a slab separation of 1.561 Å. Observe the values in the table.

6. Click now on the entry in the table to visualize the planes in the Mercury visualizer. Note that this will also open the *Packing and Slicing* window.



7. You can rotate the structure to see the alignment of molecules around the slip plane. You can see that there is a significant separation between the two slabs with potential slips in directions parallel to the plane. This structure has a high likelihood of having a slip plane and it is indeed the one indicated as plastic in the literature. Structures with such features might be preferable when compression of the particle is involved.

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	Orientation	Slab separation	Repeat distance	Offset	H-bonded	Perpendicular planes
1	(020)	1.561	10.977	-3.942	yes	

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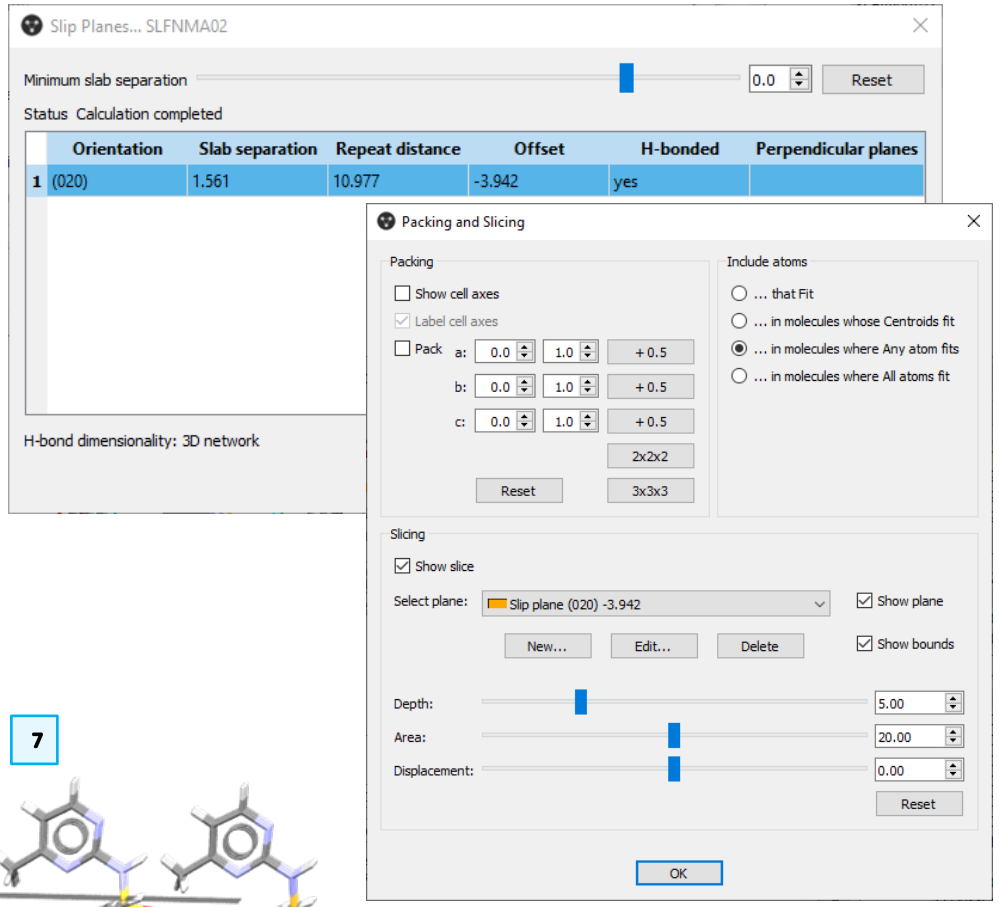

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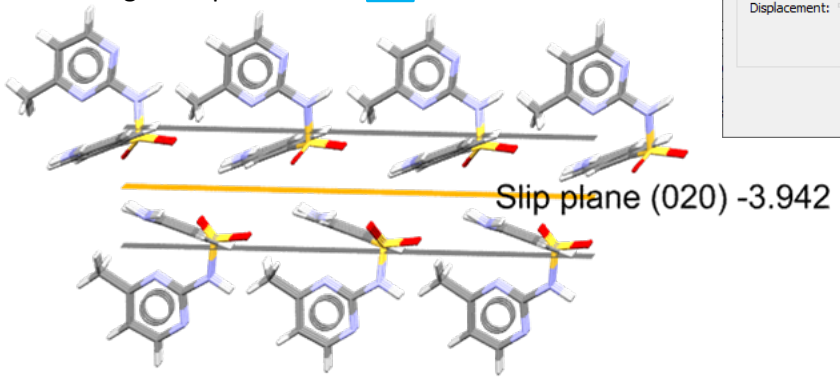


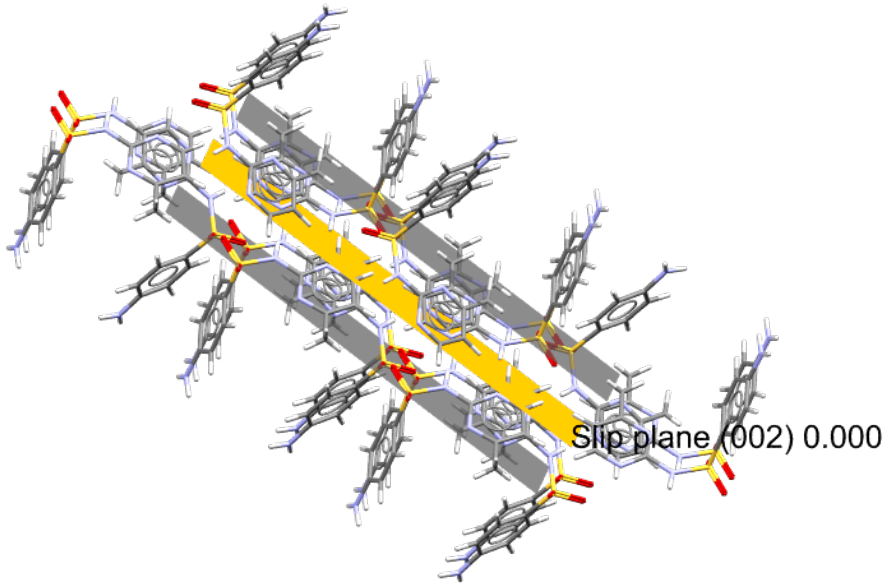
8. We will now compare this structure with the *elastic* polymorph. Open another Mercury window by clicking on the icon again (on macOS, open a terminal window and run this command: open -n -a "/Applications/CCDC/CSD_2022/mercury.app) and in the *Structure Navigator* on the right-hand side of the Mercury interface type the refcode SLFNMA01.

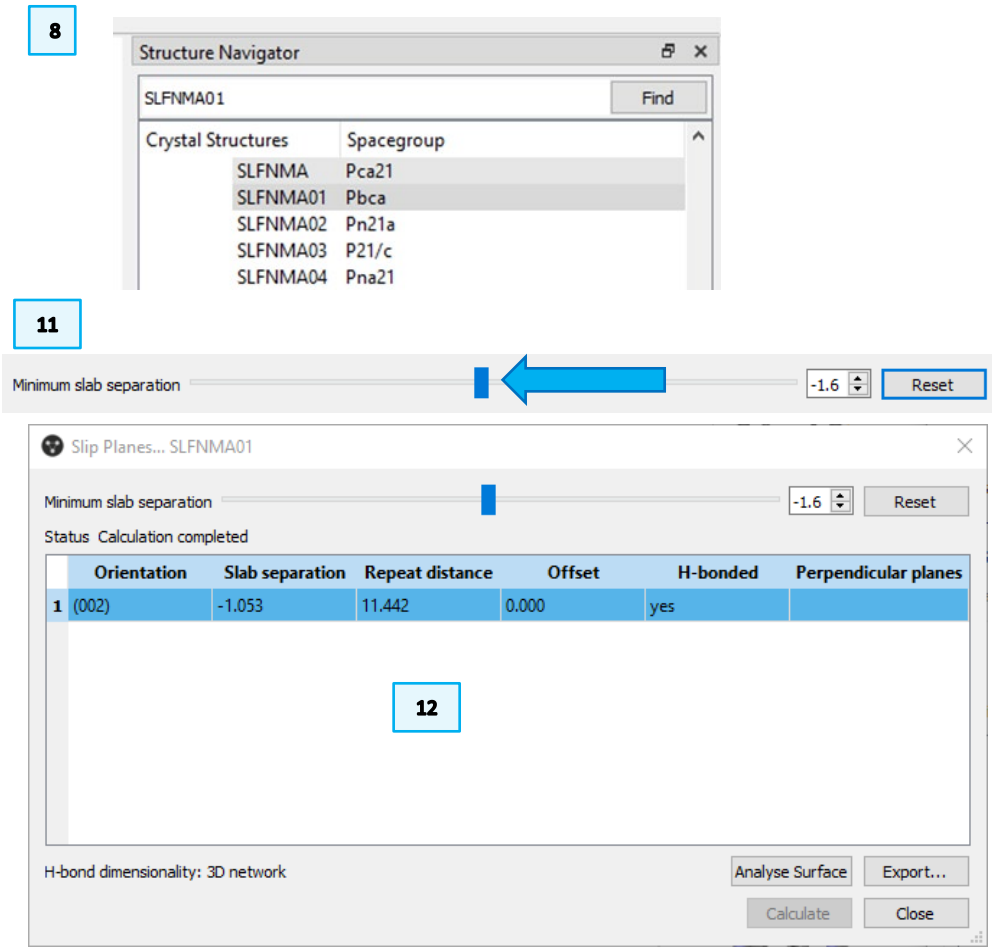
9. Re-open the slip planes menu; from the top-level menu select **CSD-Particle > Slip Planes…** as in **Step 3** above.

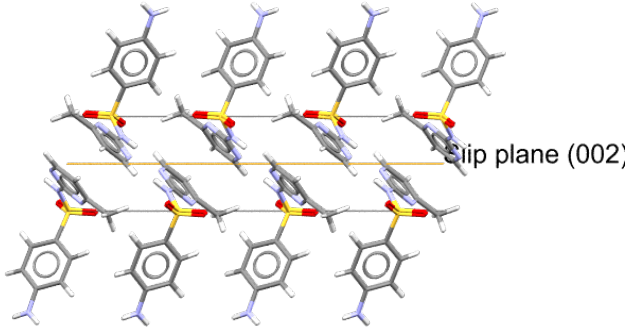
10. To start the calculation, click **Calculate** as in **Step 4** above. You will see that nothing has happened. The reason for this is that in this structure there are no potential slip planes with the minimum slab separation selected (0.0 Å).

11. Reduce the minimum slab separation by dragging the slider until the value is set to -1.6 Å. You will see in the dialog box that a new row has appeared with a slab separation value of -1.053 Å.

12. Observe the values in the table and then click on the row to visualize the plane in the structure. You will notice that for this polymorph the slabs are closer with more interlocked molecules compared to the structure analysed before. The potential slip plane appears more corrugated.



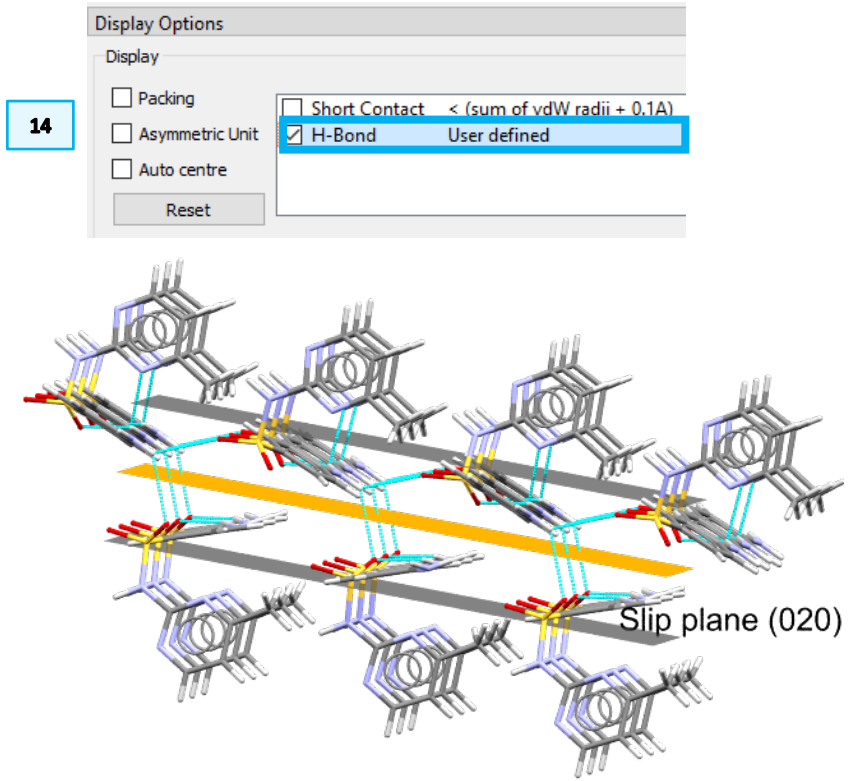




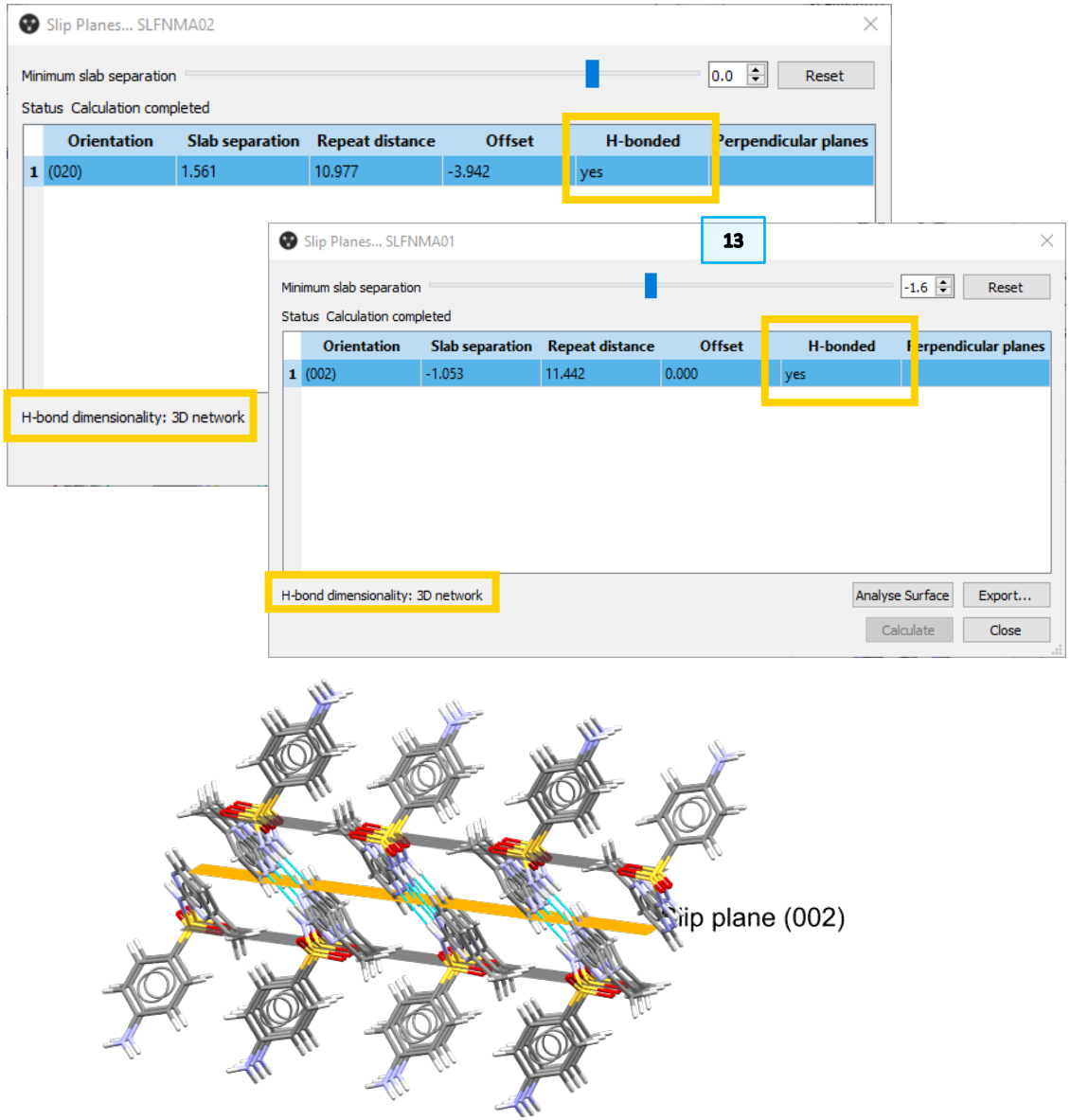
Hydrogen bonds analysis

13. For both structures, we will explore the *hydrogen bonds* network. Hydrogen bonds are indeed really important for the stability of the structure. At the bottom of the Slip Planes window, you will see *H-bond dimensionality: 3D network*; and in the table, under *H-bonded* you can read "*yes*", which means that there are hydrogen bonds across the defined slip plane.

14. Visualize hydrogen bonds by turning on H-Bonds in the *Display Options* box at the bottom of the Mercury interface.



Hydrogen bonds for the plastic deforming polymorph, CSD Entry SLFNMA02



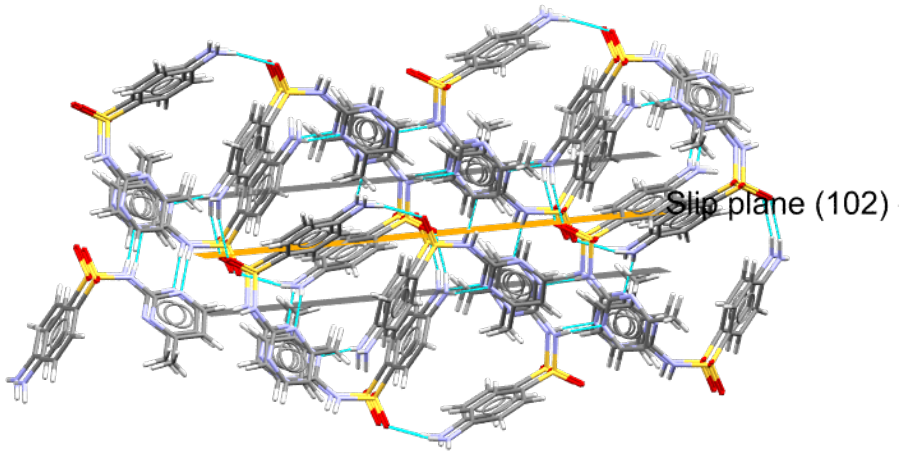
Hydrogen bonds for the elastic deforming polymorph, CSD Entry SLFNMA01

Exploring more potential slip planes

15. Go back to the Mercury window with CSD Entry SLFNMA01.

16. To bring up more potential slip planes, drag the cursor at the top of the *Slip Planes* window to lower the minimum slab separation until a value of -4.0 Å. A total of 7 planes will populate the table.

17. If you explore the potential planes, by clicking on each entry, you will notice that plane (102) is very interlocked and connected so it seems very unlikely to be a slip plane. It is thus important to analyse in detail the potential planes.



18. You will also notice that the column with *perpendicular planes* is now populated and informs of which other potential slip planes are about perpendicular to the one in analysis. This might help assess where in an elastic system there might be a flexible crystal.

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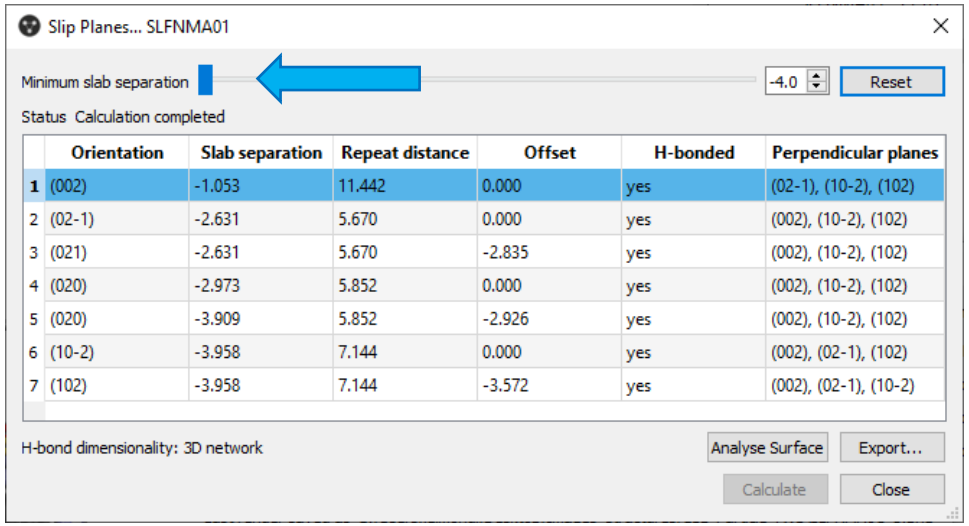


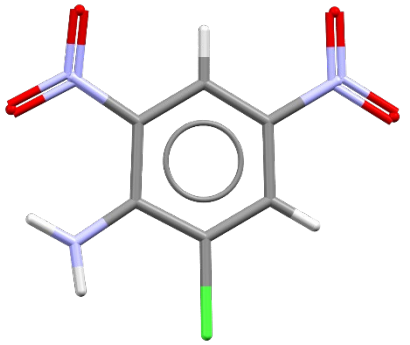
	Orientation	Slab separation	Repeat distance	Offset	H-bonded	Perpendicular planes
1	(002)	-1.053	11.442	0.000	yes	(02-1), (10-2), (102)
2	(02-1)	-2.631	5.670	0.000	yes	(002), (10-2), (102)
3	(021)	-2.631	5.670	-2.835	yes	(002), (10-2), (102)
4	(020)	-2.973	5.852	0.000	yes	(002), (10-2), (102)
5	(020)	-3.909	5.852	-2.926	yes	(002), (10-2), (102)
6	(10-2)	-3.958	7.144	0.000	yes	(002), (02-1), (102)
7	(102)	-3.958	7.144	-3.572	yes	(002), (02-1), (10-2)

Conclusion

In this example, we explored an elastic and a plastic polymorph of sulfamerazine. Using the Slip Planes tool from CSD-Particle, we were able to investigate the location and properties of potential slip planes and consider how these could be related to the experimentally determined plastic or elastic properties.

Example 2. Slip planes analysis to investigate plastic properties of polymorphs

In the previous example, we looked at polymorphs that have different elastic properties: one plastic and the other elastic. In this example, we will look at polymorphs that exhibit similar plastic behaviours, however, one is more compressible than the other due to the type of planes observed.



6-Chloro-2,4-dinitroaniline molecule from CSD Entry UCECAG02.

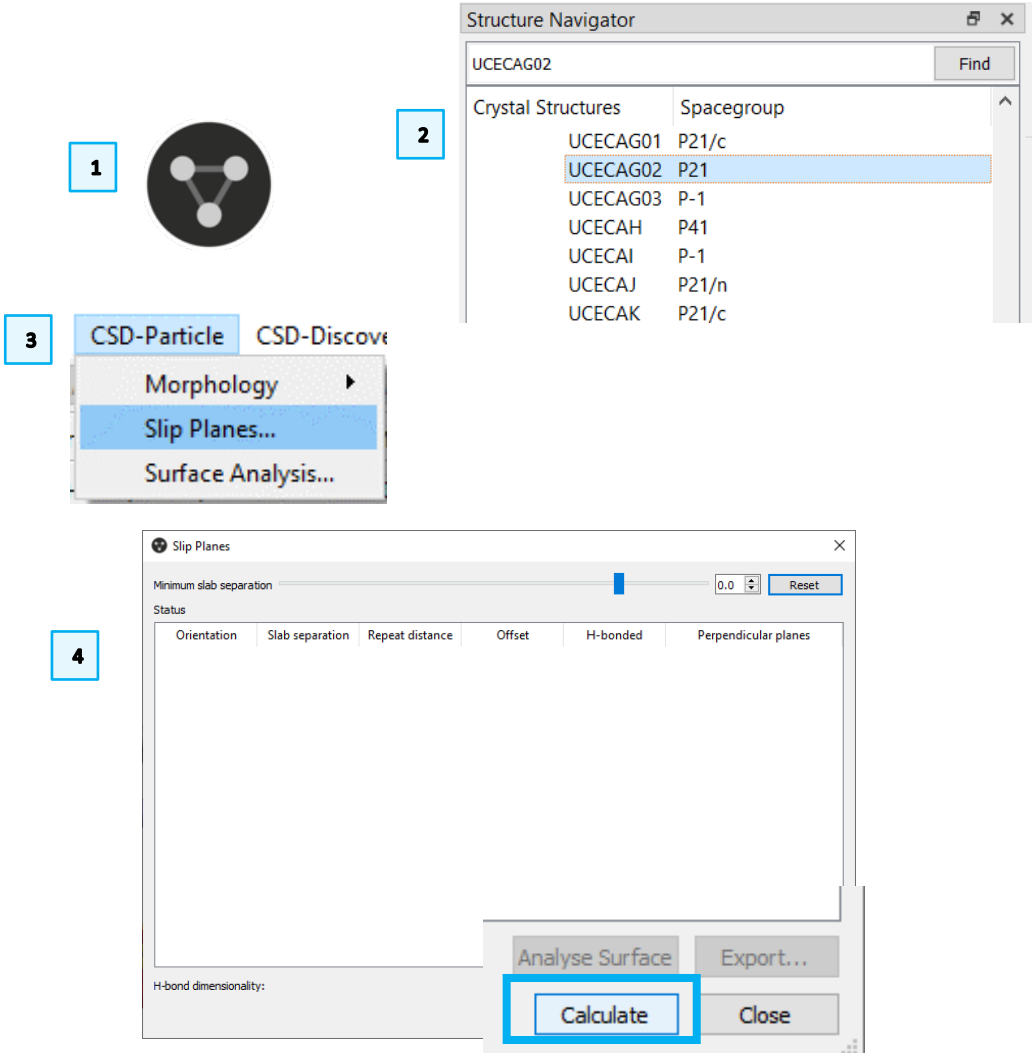
Calculation of potential slip planes

1. Open Mercury by double-clicking the Mercury icon on the desktop.

2. In the *Structure Navigator* on the right-hand side of the Mercury interface type the refcode UCECAG02 to bring up the first polymorph that we are going to investigate.

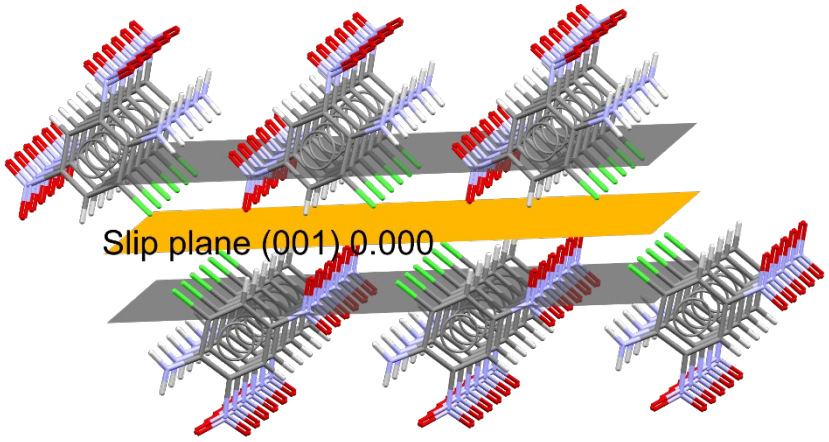
3. From the top-level menu select **CSD-Particle > Slip Planes…** to launch the *Slip Planes* window.

4. Observe that the minimum slab separation is set to 0.0 Å. To start the calculation, click **Calculate** at the bottom of the *Slip Planes* window.

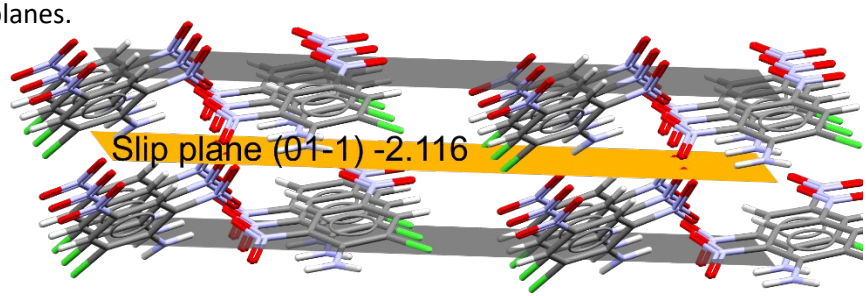


5. You will see that the table is now populated with entries representing potential slip planes with the value of slab separations. You will also notice that the Perpendicular planes have also been populated. Perpendicular planes might help assess where in a system there might be a flexible crystal. Observe the values in the table.

6. Click now on the first entry in the table to visualize the planes in the Mercury visualizer. Note that this will also open the *Packing and Slicing* window. You can move the Area slider to adjust the views in the main Mercury window.



7. You can rotate the structure to see the alignment of molecules around the slip plane. You can see that there is a significant separation between the two slabs with potential slips in directions parallel and perpendicular to the plane. This structure has a high likelihood of having a slip plane. Structures with such features might be preferable when compression of the particle is involved. You can also view a different entry; select orientation (01-1) to view the planes.



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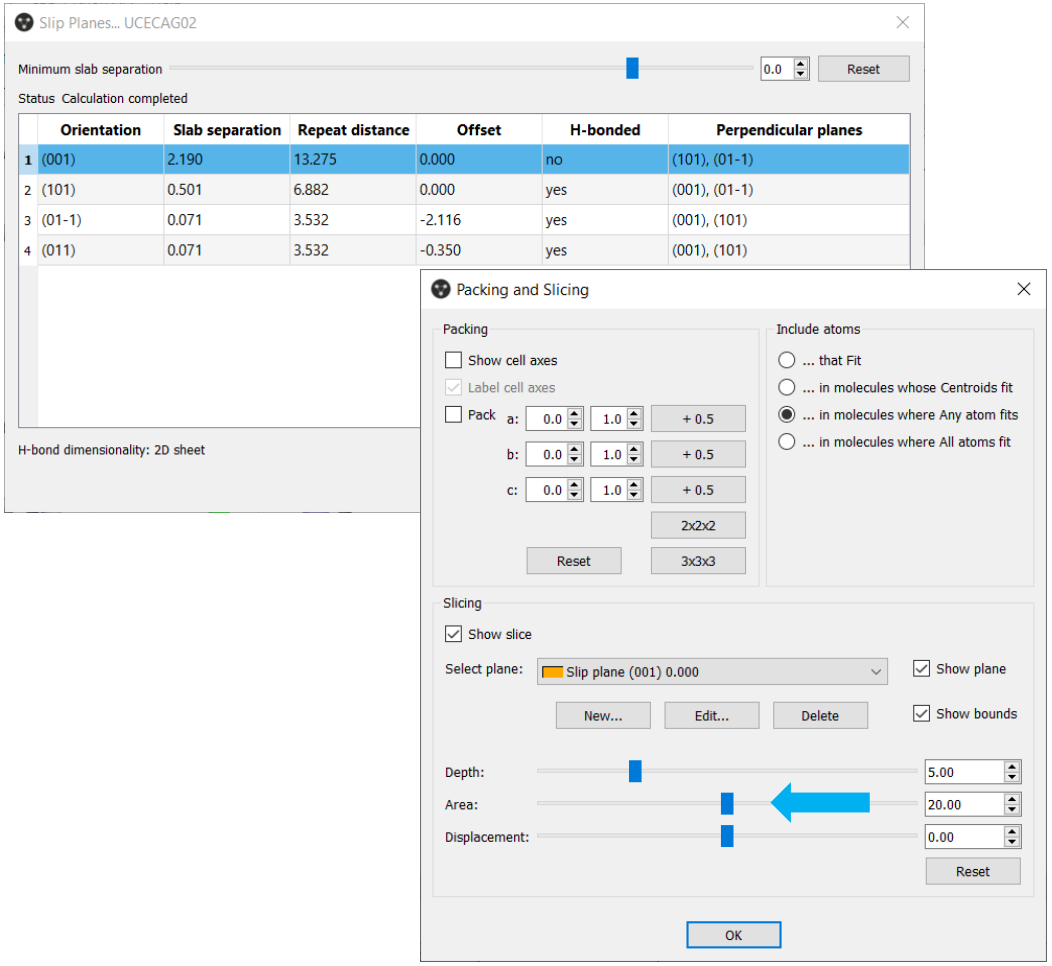
	Orientation	Slab separation	Repeat distance	Offset	H-bonded	Perpendicular planes
1	(001)	2.190	13.275	0.000	no	(101), (01-1)
2	(101)	0.501	6.882	0.000	yes	(001), (01-1)
3	(01-1)	0.071	3.532	-2.116	yes	(001), (101)
4	(011)	0.071	3.532	-0.350	yes	(001), (101)

6

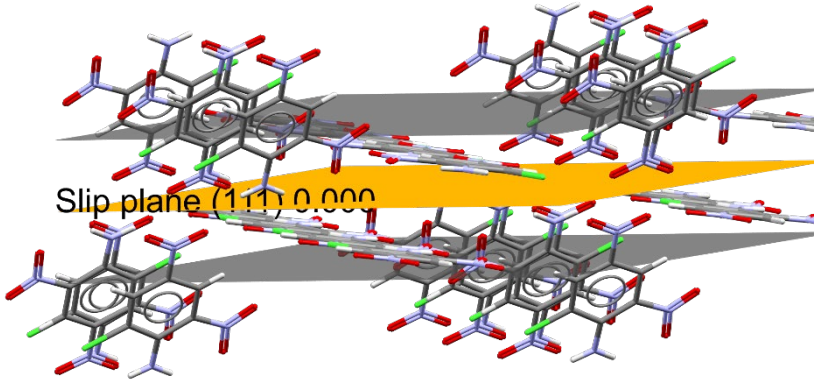


8. We will now compare this structure with the other polymorph. In the *Structure Navigator* on the right-hand side of the Mercury interface type the refcode UCECAG03.

9. If you have previously closed the *Slip Planes* window, re-open it from the top-level menu by selecting **CSD-Particle > Slip Planes…** as in **Step 3** above.

10. To start the calculation, click **Calculate** as in **Step 4** above. You will see the table populated with two entries. You will notice that there are no perpendicular planes observed in this structure.

11. Observe the values in the table and then click on each row to visualize the plane in the structure. You will notice that for this polymorph there are no perpendicular ones, only parallel ones. We can say that this polymorph is less likely to be flexible than the other.



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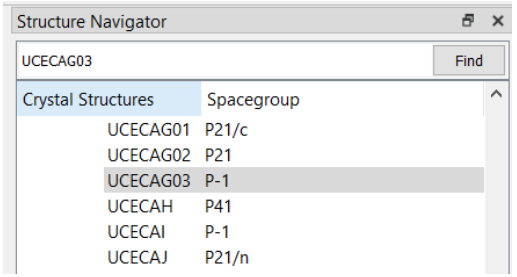

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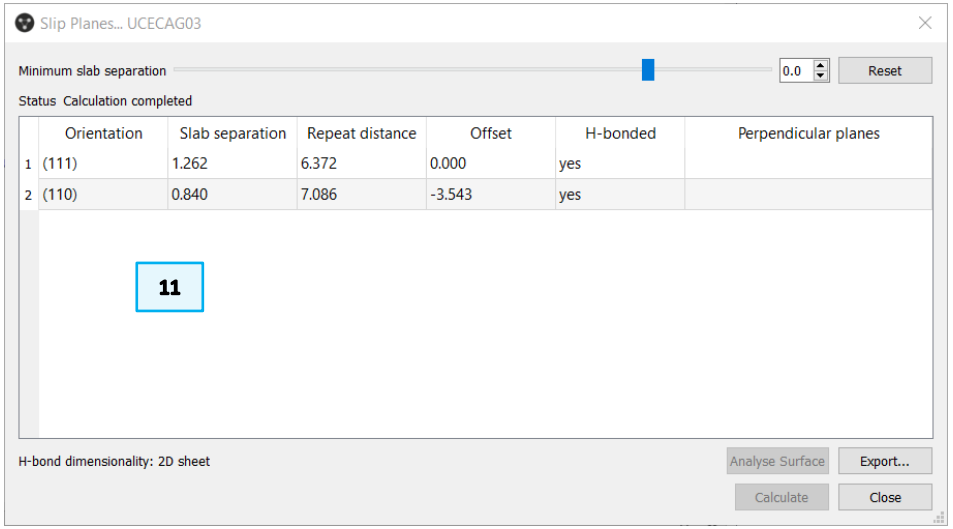

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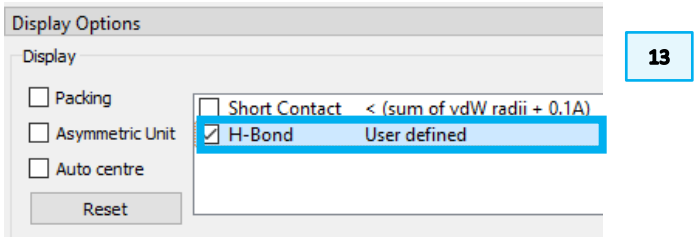
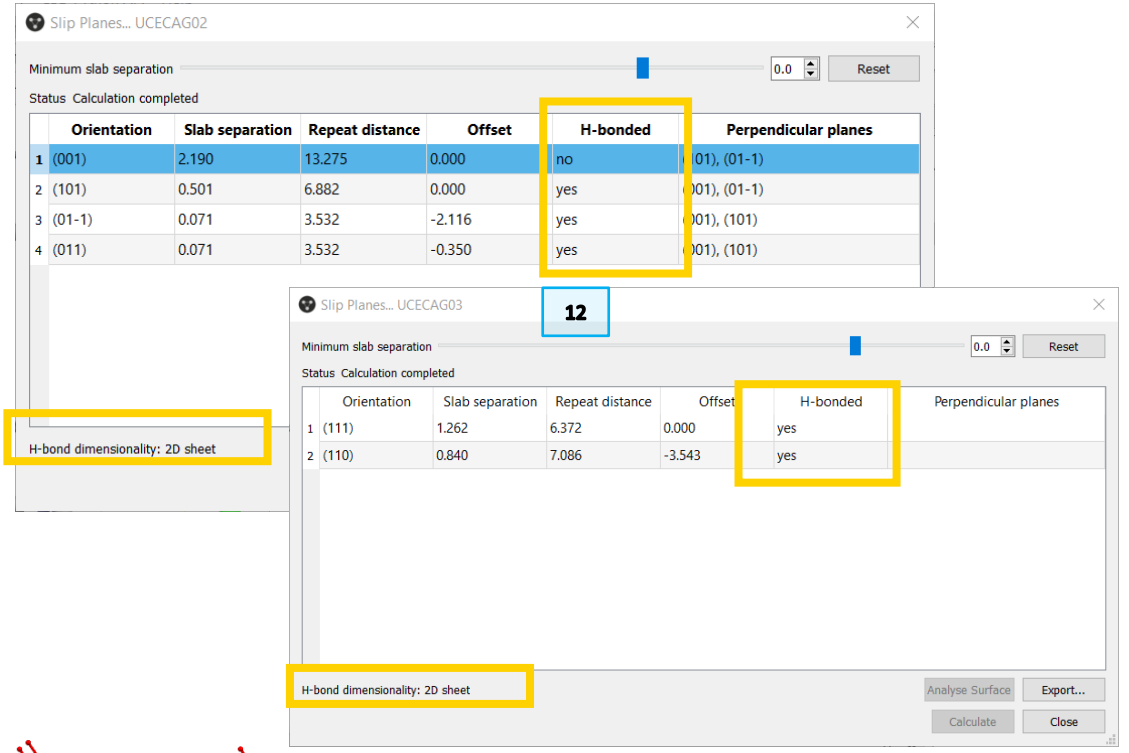
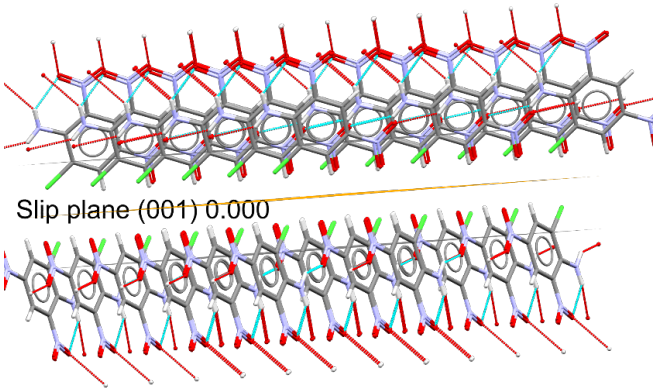
Hydrogen bonds analysis

12. For both structures, we will explore the hydrogen bonds network. Hydrogen bonds are indeed really important for the stability of the structure. At the bottom of the Slip Planes window, you will see *H-bond dimensionality: 2D sheet* for both structures. In the table for UCECAG02, under *H-bonded* you can read "*no*" for the first entry, which means that there are no hydrogen bonds across the plane. However, the other entries do exhibit hydrogen bonding for both structures

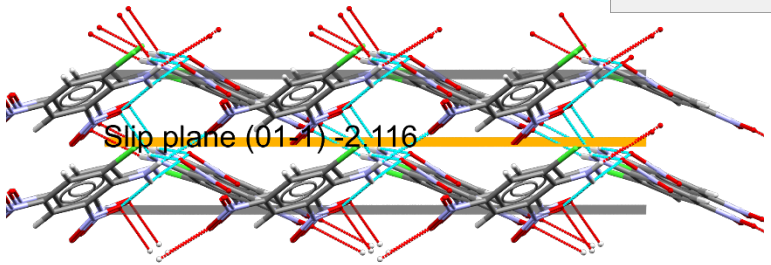
13. Visualize hydrogen bonds by turning on H-Bonds in the *Display Options* box at the bottom of the Mercury interface.



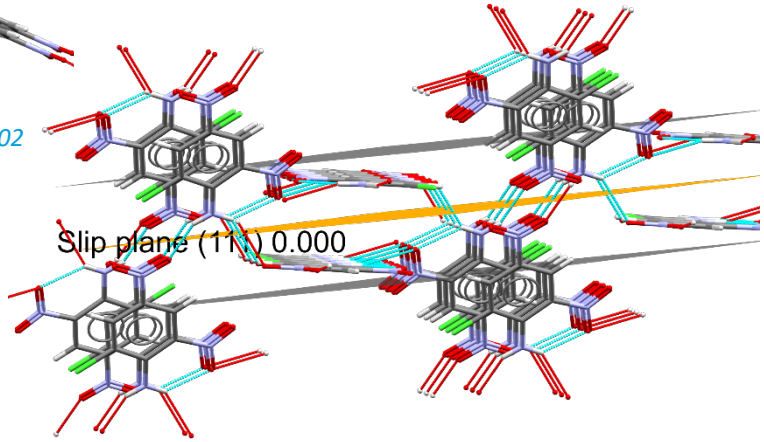




No hydrogen bonds for the first plane, the one with (001) orientation, in CSD Entry UCECAG02



Hydrogen bonds for the (01-1) orientation in CSD Entry UCECAG02



Hydrogen bonds for the second polymorph, CSD Entry UCECAG03, shown for the potential slip plane (111)

Conclusion

In this example, we used the *Slip Planes* tool from CSD-Particle to investigate polymorphs with similar behaviours, where one is more compressible than the others. We studied the potential slip planes in both polymorphs to investigate such properties.

Summary

After this workshop you should now be able to:

- Use the Slip Planes tool from CSD-Particle to explore the potential for slip planes, including, for example, to investigate elastic vs plastic behaviours.
- Calculate *hkl* surfaces and investigate their chemical and topological properties.
- Visualize hydrogen bonds in Mercury.

Next Steps

After this workshop, you can explore more exercises in the self-guided workshops available in the CSD-Particle workshops area on our website. We suggest trying the Surface Analysis with CSD-Particle Tools workshop.

Feedback

We hope this workshop improved your understanding of the use of CSD-Particle tool for exploring plastic and elastic properties of polymorphs and you found it useful for your work. As we aim to continuously improve our training materials, we would love to hear your feedback. Follow the link on the workshop homepage or click on this link to a survey, it will take less than **5** minutes to complete. The feedback is anonymous. You will be asked to insert the workshop code, which for this self-guided workshop is PAR-001. Thank you!

Reading suggestions

You might find the following publications of interest:

- "Particle Informatics": Advancing Our Understanding of Particle Properties through Digital Design, ***Cryst. Growth Des.***, 2019, **19**, 9, 5258–5266 - https://doi.org/10.1021/acs.cgd.9b00654
- Elastically flexible molecular crystals, ***Chem. Soc. Rev.***, 2021, **50**, 11725-11740 - https://doi.org/10.1039/D1CS00469G

Glossary

Elastic vs Plastic

An elastic material is a material that after compression can return to its initial shape and size once no more force is applied to it.
On the other hand, a plastic material would retain the deformation after the force has been removed.

Hydrogen Bonds

Hydrogen bonding occurs between donor-acceptor interactions involving hydrogen atoms. The H-bond interactions are classified as: strong (mostly covalent), moderate (mostly electrostatic) and weak (electrostatic). Their strength is observed to be between 12 and 30 kJ/mol.

Minimum Slab Separation

Potential slip planes will only be shown if the slab separation value is greater than the minimum slab separation which is 0 Å. The slab distance is the shortest distance between slabs of molecules on either side of this slip plane (Å).

Perpendicular Planes

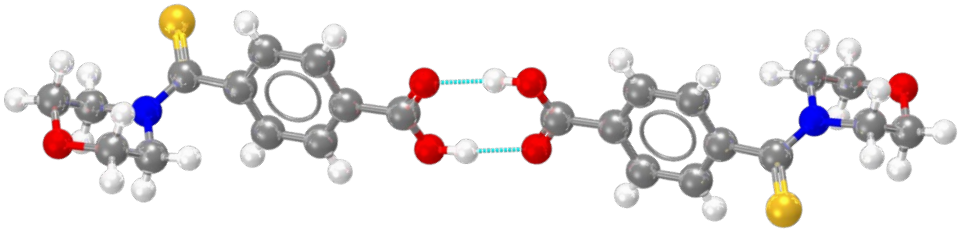
The *Perpendicular Planes* column in the Slip Planes table contains a list of any potential slip planes >45° from the given plane.

Polymorph

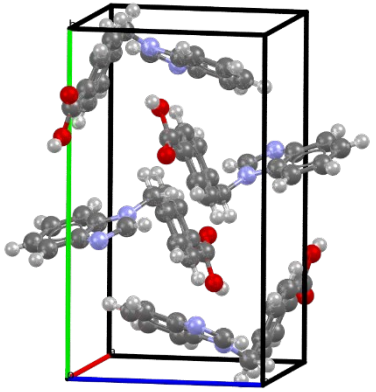
Polymorphism is the occurrence of two or more crystalline forms of the same substance. Where available, polymorph information can be displayed for Cambridge Structural Database (CSD) structures. Structures known to be polymorphic contain comments which include the word polymorph (when reported by the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

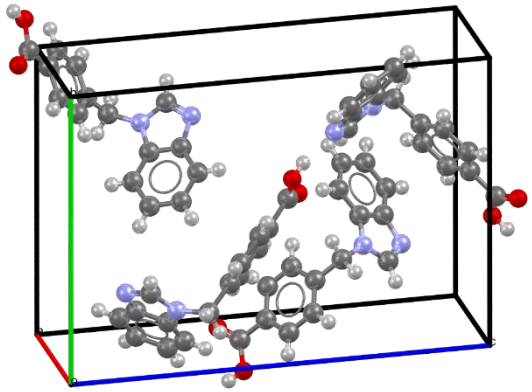
Slip Planes

Slip planes represent planes in a crystal structure along which a slip can take place.
Please note that in CSD-Particle, the Slip Planes functionality identifies potential slip planes in a crystal structure.

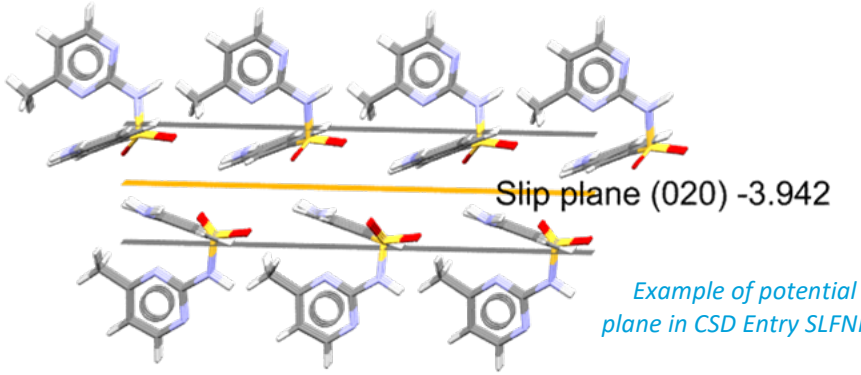


In light blue, example of hydrogen bonds for refcode MULWIC.





Example of polymorphic structures of 4-(1H-Benzimidazol-1-ylmethyl)benzoic acid: the monoclinic polymorph (CSD Entry ABADIS) at the top, and the orthorhombic polymorph (CSD Entry ABADIS01) on the right.



Example of potential slip plane in CSD Entry SLFNMA02.