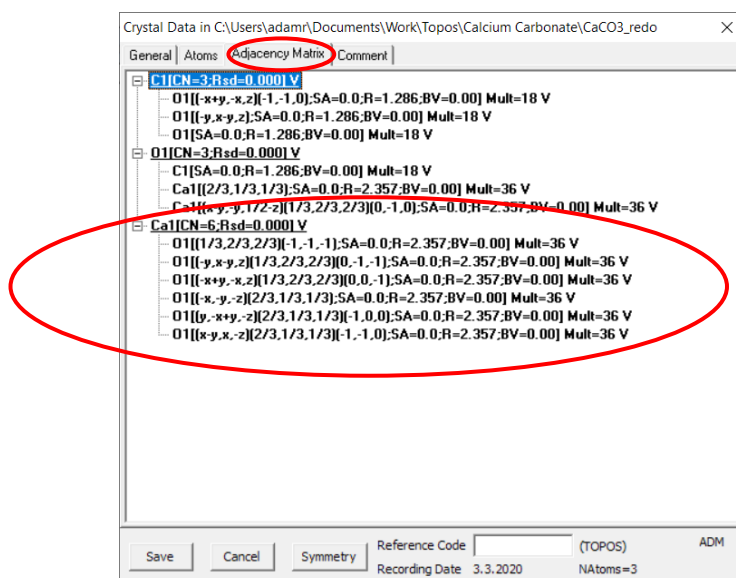


Setting Up and Visualising Interactions With *ToposPro*

This step-by-step guide will demonstrate methods to obtain and visualise an adjacency matrix for a set of interactions between molecular / ionic species for *CrystalGrower* using *ToposPro*.

Firstly, to check a calculated adjacency matrix you must double-click a database entry / the CIF file which has been read into *ToposPro*, and navigate to the “Adjacency Matrix” tab.

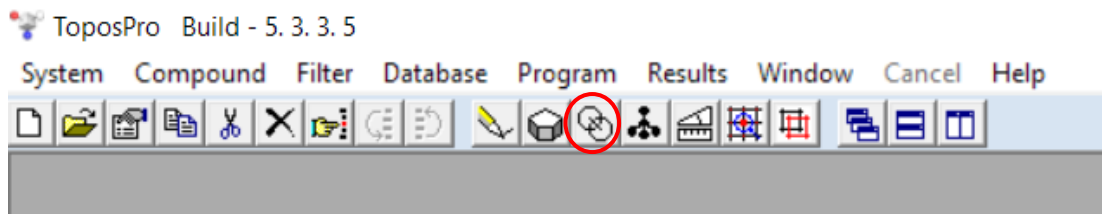


All detected interactions in the crystal structure are shown, with each bonded atom expandable into a list showing which atoms they are connected to and their interaction type. **Bold** – Valence bond, **Blue** – Hydrogen bond, **Red** – Specific bond, Black but not bold – van der Waals interaction and, **Crossed** – No bond / manually removed bond. All interactions types can be changed by right clicking the interaction, selecting “Change Type” and choosing a new interaction type. *Note that this will also change all symmetry related interactions.*

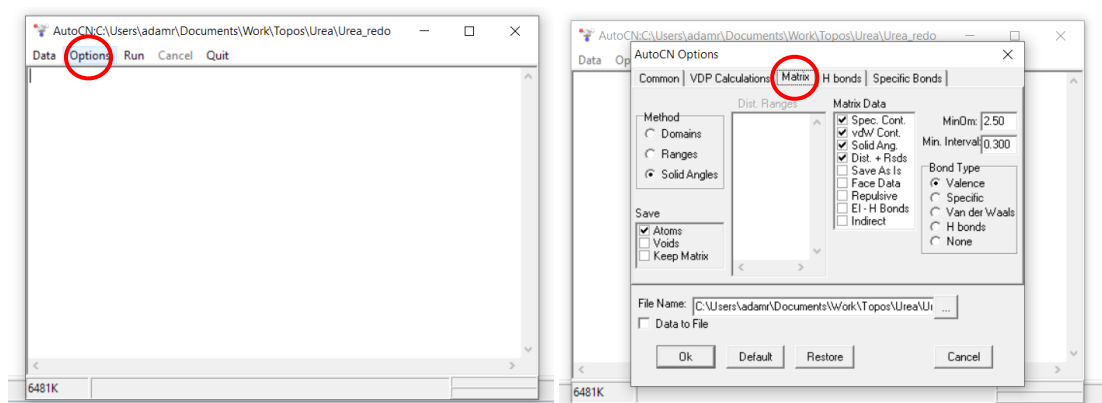
Setting up the adjacency matrix is **crucial** and will determine the connectivity of your crystal net for generating your *CrystalGrower* input files. Presented here are multiple methods for calculating an adjacency matrix correctly.

Method 1: With *AutoCN*

- 1.) Select the database entry / CIF file you want to calculate the interactions for.
- 2.) Open *AutoCN* (click the symbol with two overlapping circles or **CTRL+N**)



- 3.) Select Options and navigate to the Matrix tab.



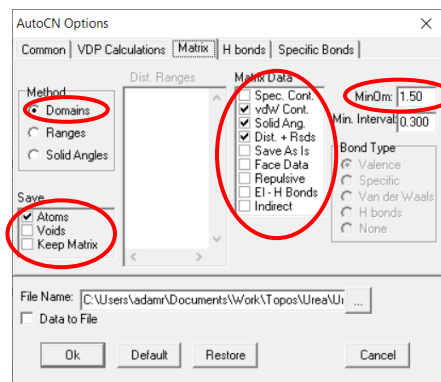
- 4.) Three methods exist for calculating the interactions between crystal species (further information on the algorithms behind each calculation method can be found here: <https://topospro.com/software/topospro/manual/details-of-the-autocn-algorithms/>):
 - a. **Domains** – Most versatile, interactions are defined by their contribution to the molecular Voronoi-Dirichlet polyhedron (VDP). Radii of atoms are adjusted based on pairs of bonded atoms in the crystal structure (e.g. metal to non-metal vs. non-metal to halogen etc.). Stronger interactions have larger faces and contribute more to the overall Voronoi Dirichlet Polyhedron (VDP) i.e. they will have a larger solid angle (Ω). MinOm (minimum omega – Ω) is the cut-off point for considering interactions, weaker interactions have a lower Ω value. Hydrogen bonds and van der Waals interactions are readily identified.
 - b. **Solid Angles** – Also versatile, interactions are defined in a similar way to Domains, however the radius of each atom type is kept constant and not adjusted based on bonded atom pairs. Interactions are only defined by their face contribution to the overall VDP.
 - c. **Ranges** – Most control over specific interactions, but risks being used arbitrarily. Interactions are specified between atoms and distances are also specified. Can be used to create an adjacency matrix manually with all

interactions defined by the user. Useful for nets with user defined “dummy” nodes e.g. molecule centroids.

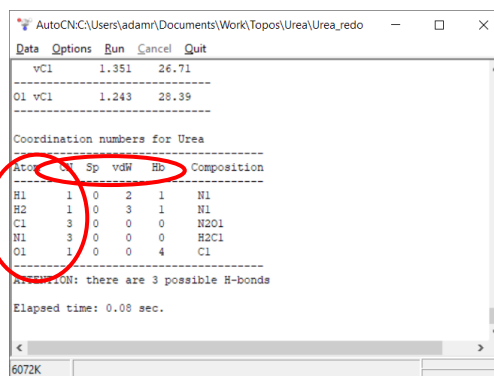
- General rule – first try Domains and vary MinOm. If you’re picking up too many H-bonds and vdW bonds, try Solid Angles and vary MinOm. Finally, if you still have issues, save the generated adjacency matrices from Domains or Solid Angles by selecting “keep matrix” then add the missing interactions with Ranges (or try making the adjacency matrix from scratch with Ranges).

5.) For **Domains**:

- Select the Domains option in “Method”.
- Ensure Atoms is ticked under the “Save” option.
- Ensure vdW Cont., Solid Ang., and Dist + Rds are ticked. (Tick Spec. Cont. if you have specific bonds in your structure).
- Changing MinOm will include or exclude weaker interactions. Higher MinOm only includes stronger interactions.



- The results window will display the coordination numbers for the atoms and their types.



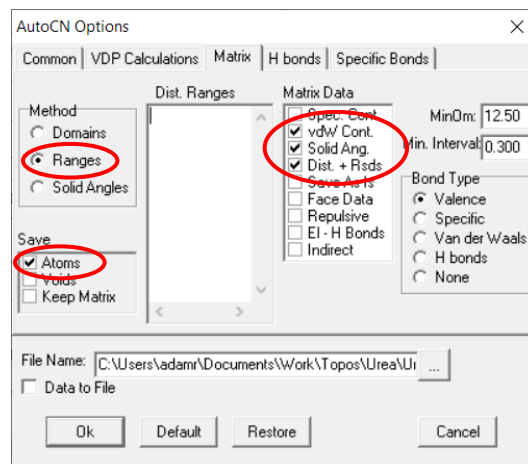
Atom	CN	Sp	vdW	Hb	Composition
H1	1	0	0	1	N1
H2	1	0	0	1	N1
C1	3	0	0	0	N2O1
N1	3	0	0	0	H2O1
O1	1	0	0	4	Cl

ATTENTION: there are 3 possible H-bonds

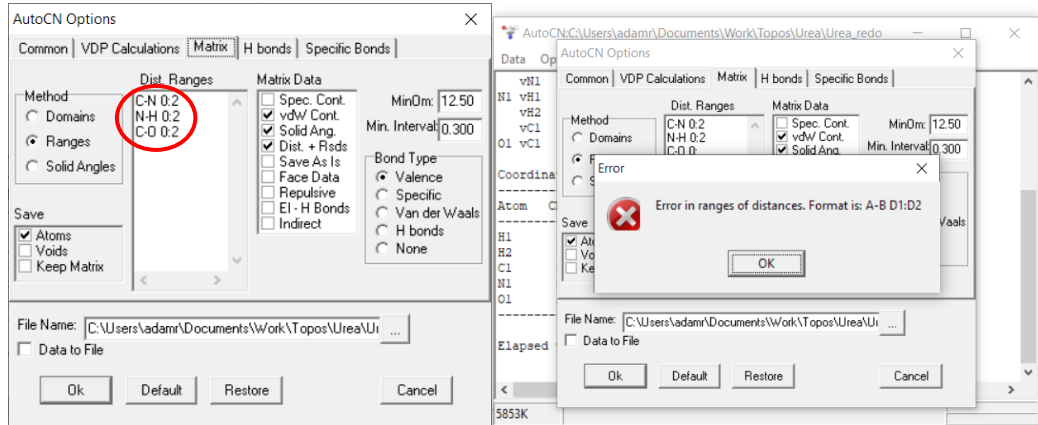
Elapsed time: 0.09 sec.

7.) For Ranges:

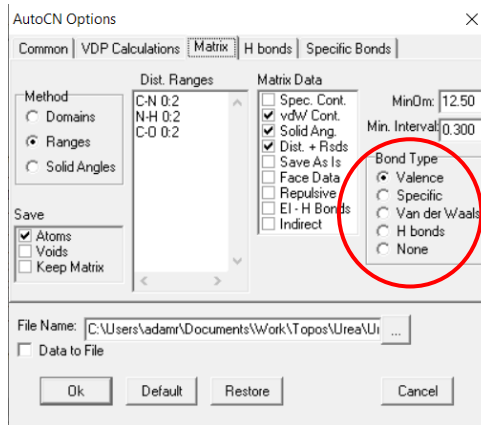
- Select the Ranges option under “Method”.
- Ensure Atoms is ticked under the “Save” option.
- Ensure vdW Cont., Solid Ang., and Dist + Rds are ticked. (Tick Spec. Cont. if you have specific bonds in your structure).



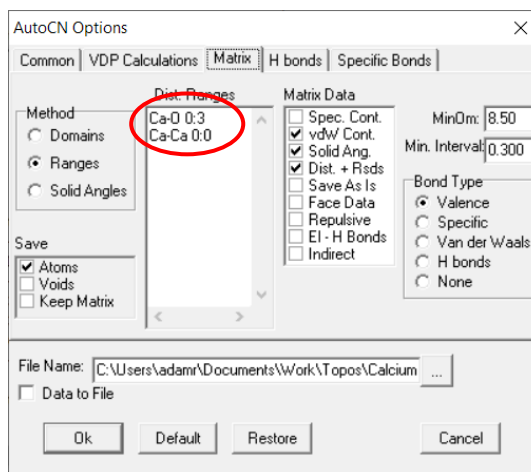
- Select the “Dist. Ranges” box.
- Type in the atoms you want to add bonds between, and the range of distances you want these bonds to extend over (in Angstroms). The format is:
Atom1-Atom2 Start Range : End Range - Topos will ask you to correct this if it's incorrectly formatted. E.g. Na-Cl 0:10 will create bonds between all sodium and chloride ions in the structure that are within 10 Å of each other, set to whatever bond type chosen under “Bond Types”.



- The bond type selected under the “Bond Type” option will be assigned to the interactions found at the selected distances. The output window of *AutoCN* will not change, but the adjacency matrix will be updated when checked by double-clicking the database entry.

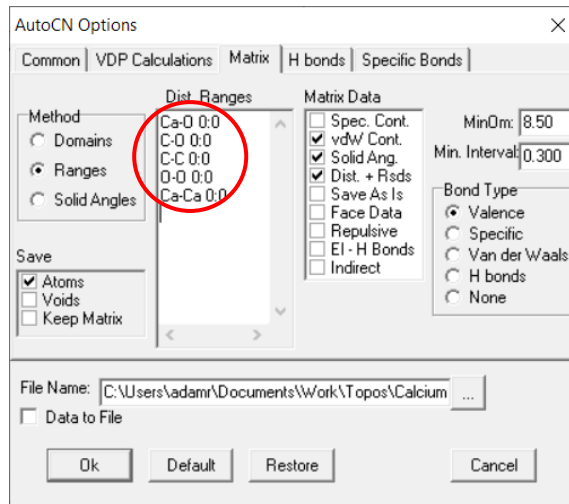


- To turn off certain bonds, users can insert a distance range of 0:0. E.g. Ca-Ca 0:0 would ignore all Ca to Ca bonds in a structure.



8.) A very useful option to employ with all the above methods is the “Keep Matrix” option. This will retain the last calculated adjacency matrix and add the newly calculated bonds to it. This is a flexible method of adding new connections to the matrix and assigning them a specific type.

- Using “Ranges” and calcite as an example:
- All bonds are disabled by setting their distance ranges from 0:0.



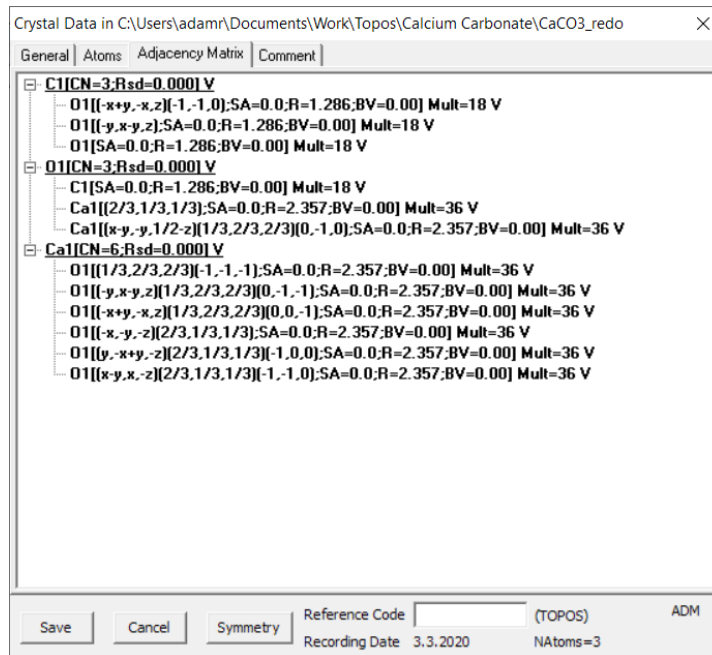
- Ca-O and C-O bonds are set to a short range (3 Å and 2 Å, respectively) and set to valence to pick up the main ionic interactions.

The screenshot shows the 'AutoCN Options' dialog box with the 'Matrix' tab selected. In the 'Dist. Ranges' list, 'Ca-O 0:3' and 'C-O 0:2' are circled in red. In the 'Bond Type' section, 'Valence' is selected and circled in red. The 'File Name' field contains 'C:\Users\adam\Documents\Work\Topos\Calcium ...'. To the right, the output window shows the following data:

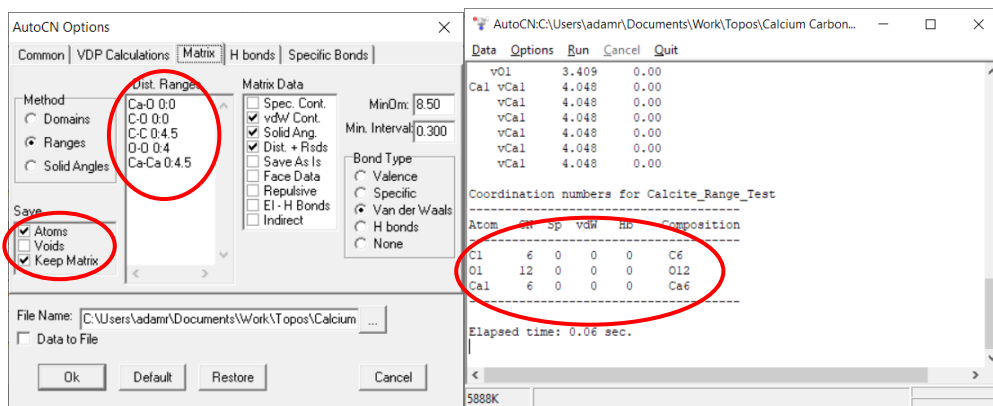
Atom	CN	Sp	vdW	Hb	Composition
Cl	3	0	0	0	O3
O1	3	0	0	0	ClCa2
Ca1	6	0	0	0	O6

The output window also shows 'Elapsed time: 0.04 sec.' and '5991K'.

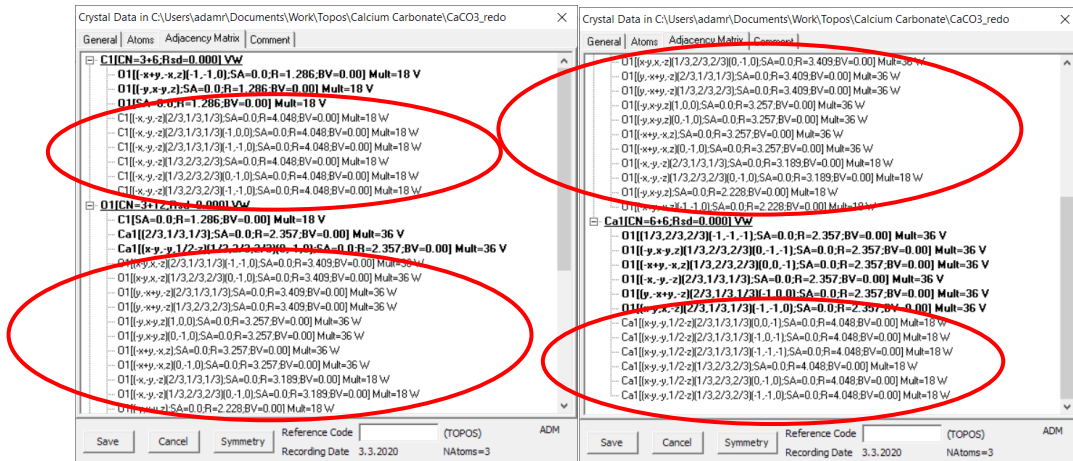
- The following adjacency matrix is obtained with C coordinated to 3 O's and Ca coordinated to 6 O's:



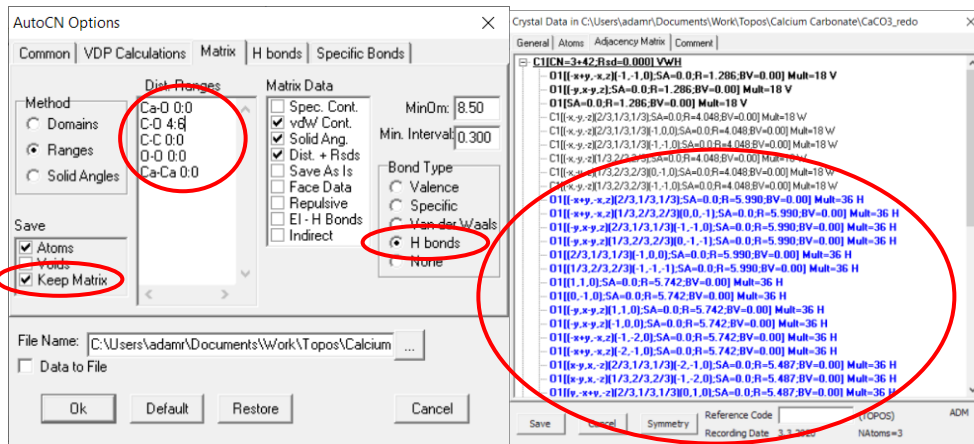
- If longer range interactions are required, e.g. van der Waals interactions, they can be added on top of the current matrix. Considering Ca-Ca, C-C and O-O long range interactions for example.
- Selecting the “Keep Matrix” checkbox under the “Save” options, and assigning the required distances (remembering that a range of 0:0 will ignore interactions) will lead to a new set of interactions being discovered:



- While the *AutoCN* window implies that the previous interactions were replaced and that the new interactions were assigned as valence instead of vdW as requested, checking the Adjacency Matrix tab when double-clicking a database entry shows that the connections have in fact been added and assigned the type of vdW.



- This action can be repeated to add further connections to the matrix. E.g. adding long range C-O “H-bonds”:

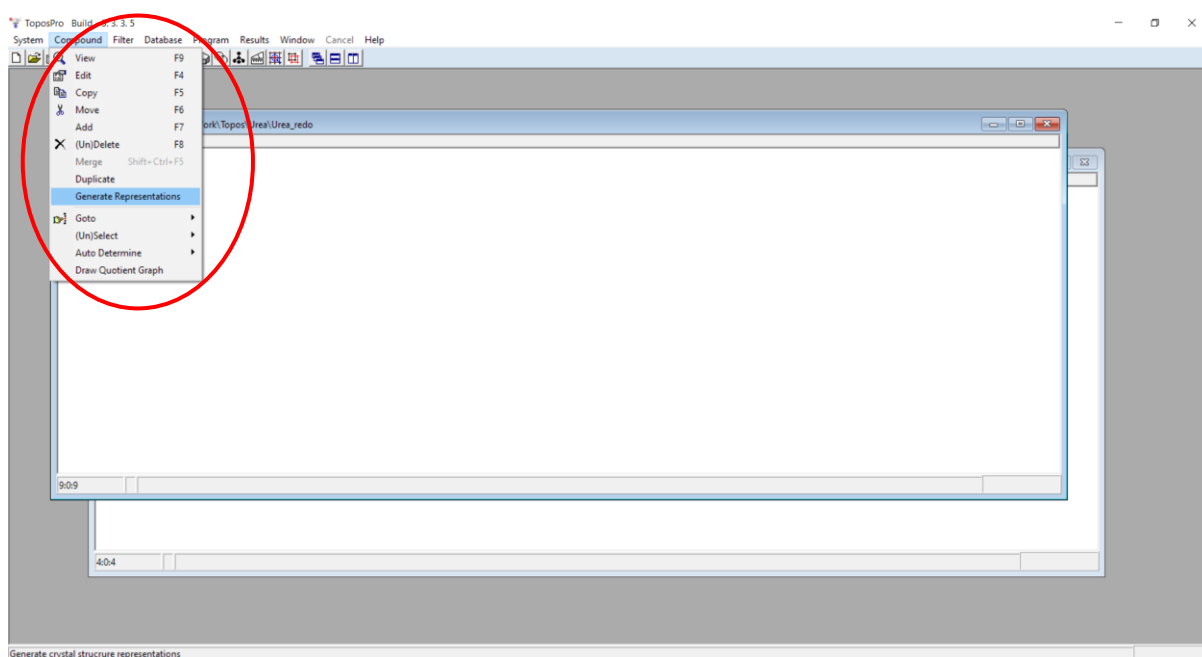


- The “Keep Matrix” option can be used with any and all combinations of the previously discussed “Method” options i.e. Domains, Ranges and Solid Angles.

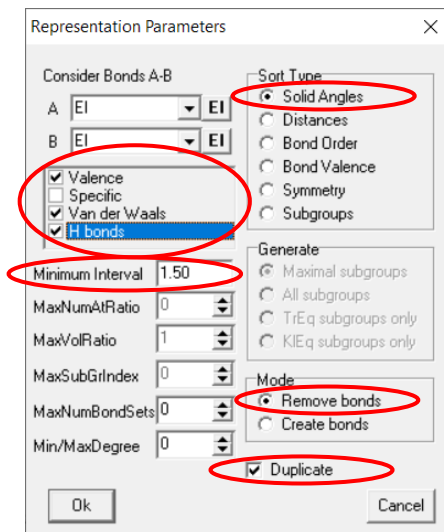
Method 2: Using Generate Representations (only available in Full Version of ToposPro)

This route requires first using *AutoCN* to calculate some description of the connectivity in the crystal structure. Use a method from above and aim to overestimate the connectivity (i.e. include even the weakest interactions). *Generate Representations* is a quick route to produce several separate database entries with varying interaction strengths.

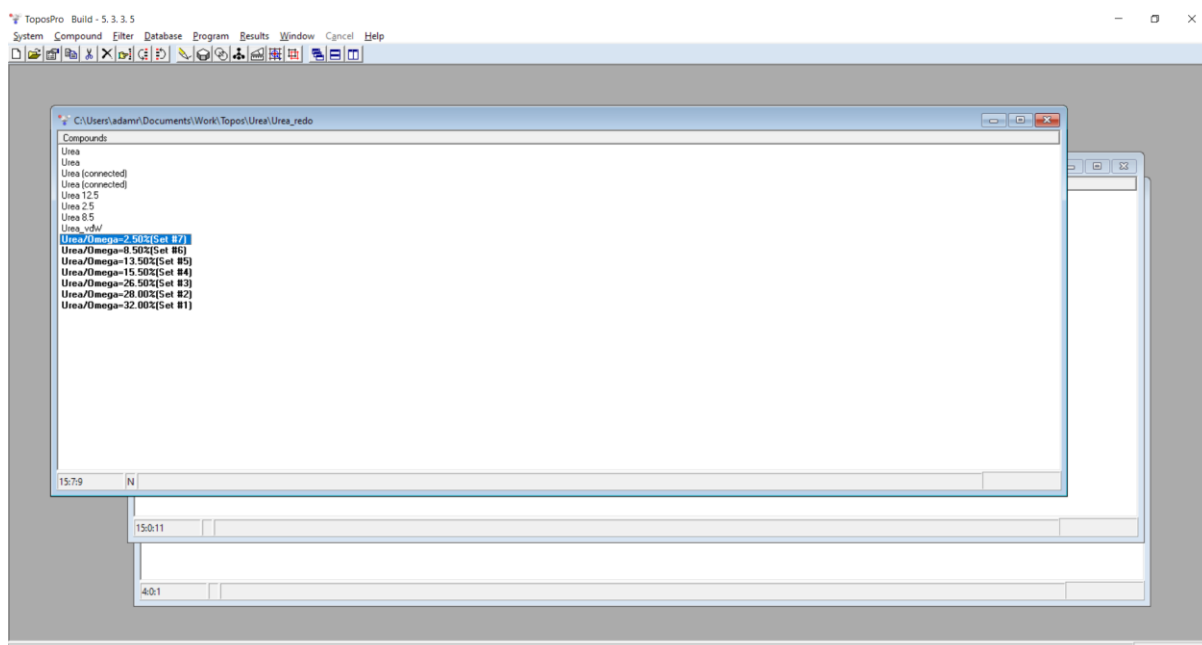
- 1.) Import your CIF file and run *AutoCN* using method 1 to estimate the connectivity.
- 2.) Click “Compound” and select “Generate Representations”



- 3.) Select the bond types that you wish to consider and select Solid Angles as the Sort Type. Set the minimum interval to a relatively low number (this is the interval that minimum omega will increment upwards by when searching for interaction sets). Large numbers may miss out on some interaction sets. Also set the mode to remove bonds. To create the new files in the same database, you must also tick Duplicate.

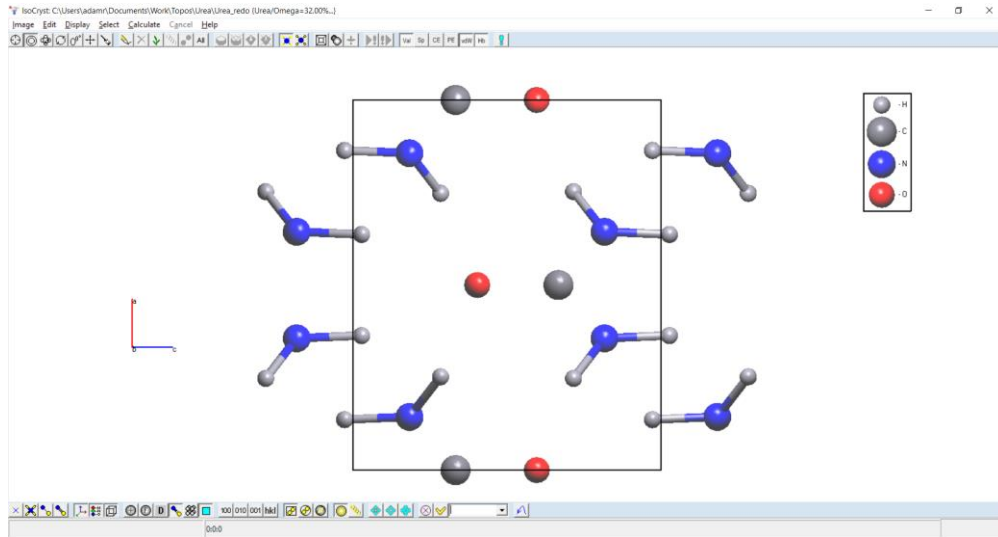


- 4.) Press OK and the window will close, this will then generate several database entries with varying sets of interactions between crystal species.

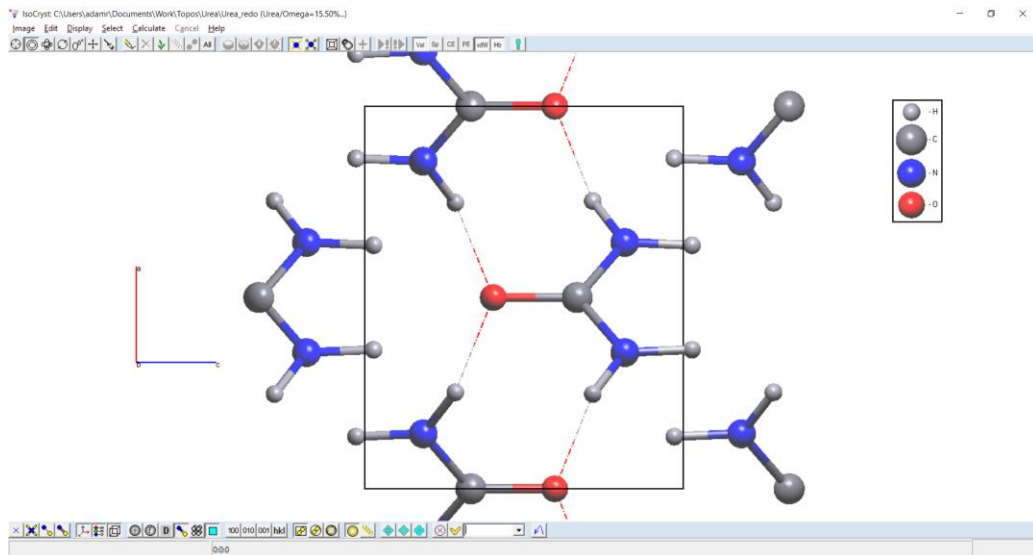


5.) The Omega value for each file is equal to the lowest solid angle it will class as an interaction. The higher values will only include the strongest of interactions, while the lowest will include all of the weaker interactions (as well as the stronger ones). E.g. some example cases for urea:

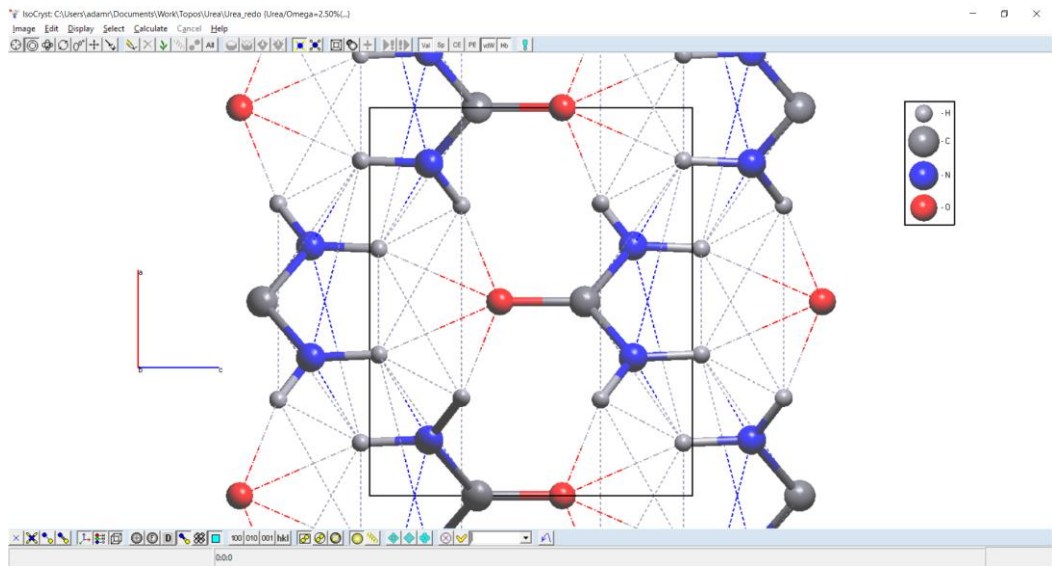
- Omega = 32.00% even ignores the longer intramolecular valence bonds.



- Omega = 15.50% includes the stronger intermolecular interactions (e.g. H-bonds)

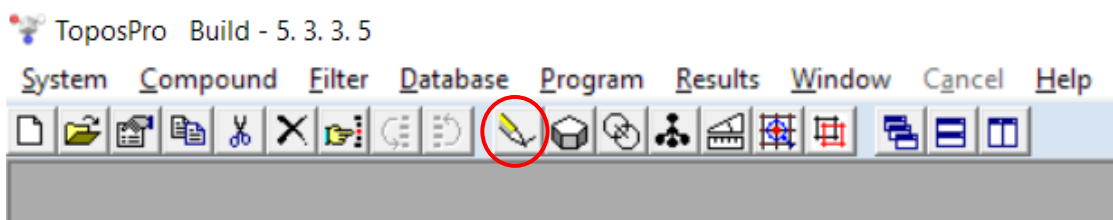


- Omega = 2.50 % includes the weakest intermolecular interactions (e.g. long range vdW interactions).



Investigating Molecular Connectivity

Users can investigate the calculated connectivity for the crystal structure using the visualisation package within *ToposPro – IsoCryst* - (**CTRL + I**) / pencil symbol on the toolbar.



Using the Grow key - (**CTRL+W**) / plant symbol on the toolbar - will grow the structure based on the currently selected atoms and bond types. Turning off bond types will not allow the structure to grow through these connections. If no atoms are selected, then the structure will behave as if all atoms are selected when pressing the grow key.



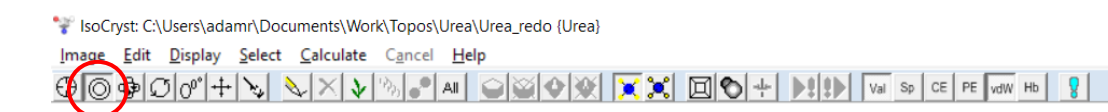
The scene can be rotated in the XY plane or the Z plane with the Rotate and Z-Rotate tools, respectively:



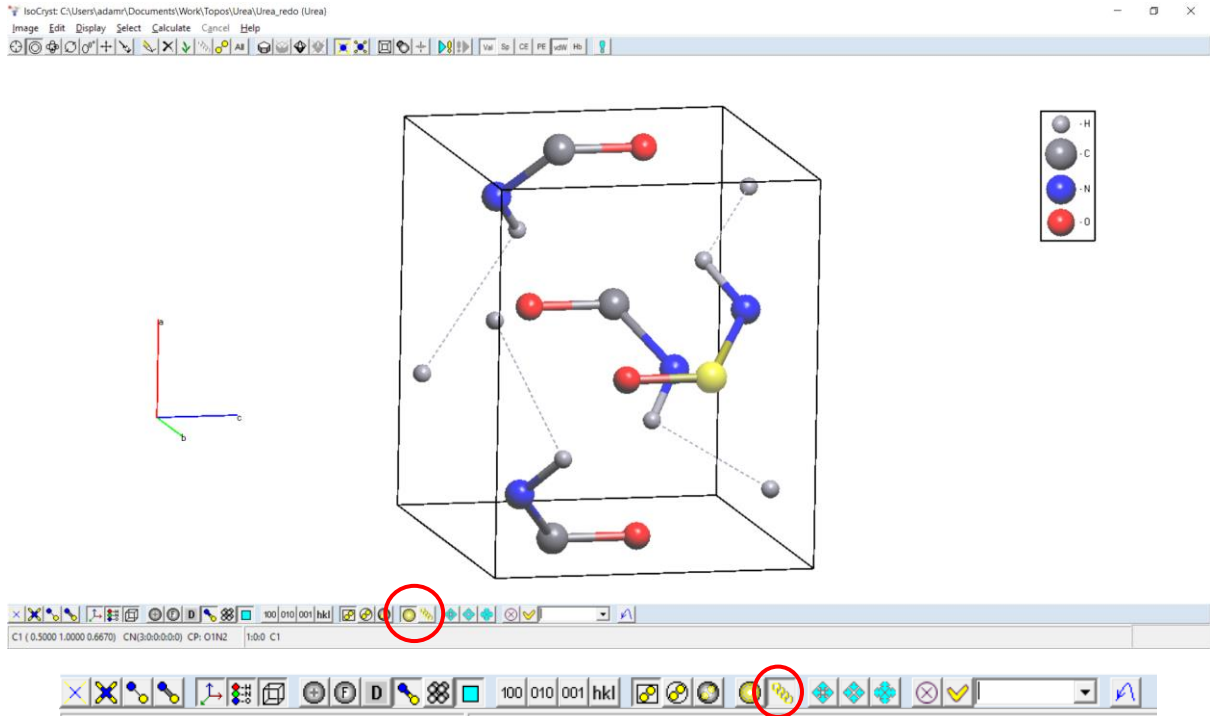
And can be translated in the Z and XY plane by the Magnify / Shrink and Translate tools, respectively:



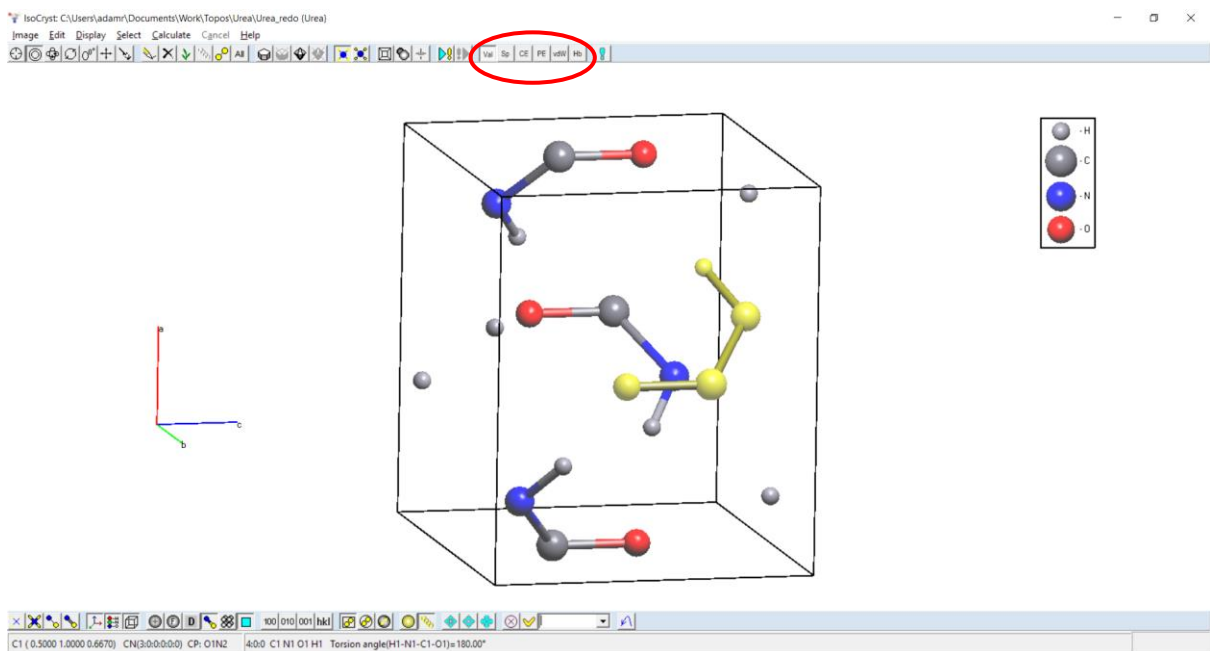
Atoms can be selected with the Select option. Once enabled, left clicking will select an atom and right clicking will deselect an atom.



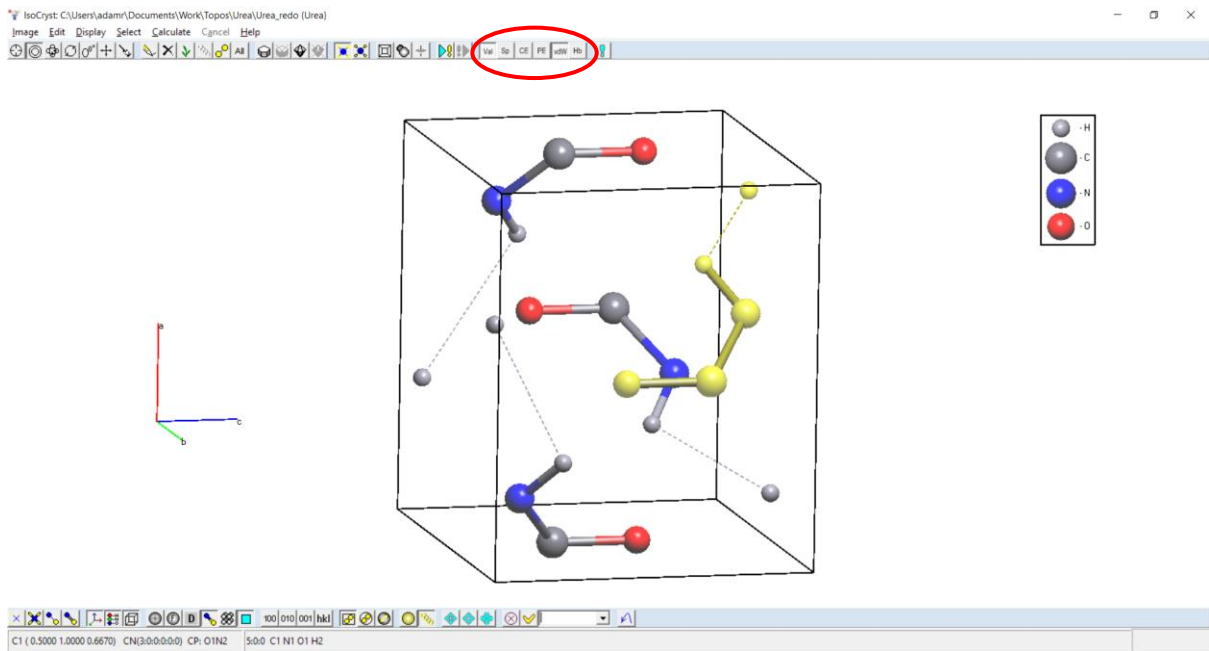
If the “Select Polymeric Chain” option is selected in the bottom toolbar, then all atoms connected by the enabled bond types will be selected. This option is useful for selecting all molecules linked by interactions.



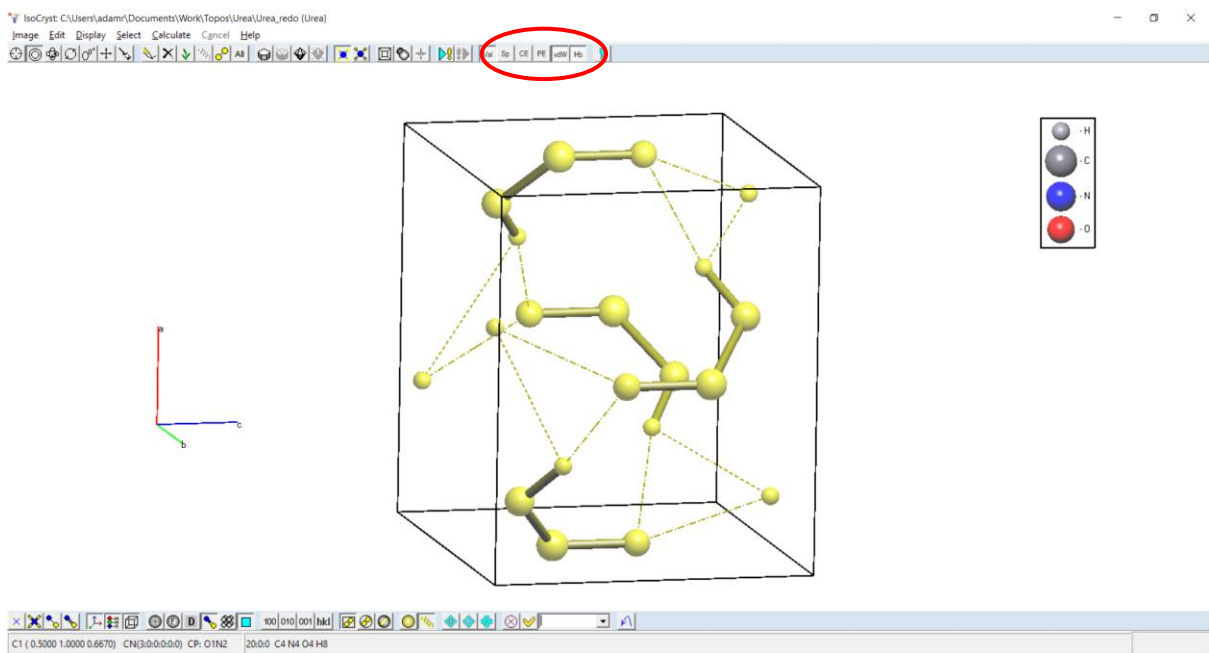
e.g. Urea linked only by valence bonds:



vdW bonds only:



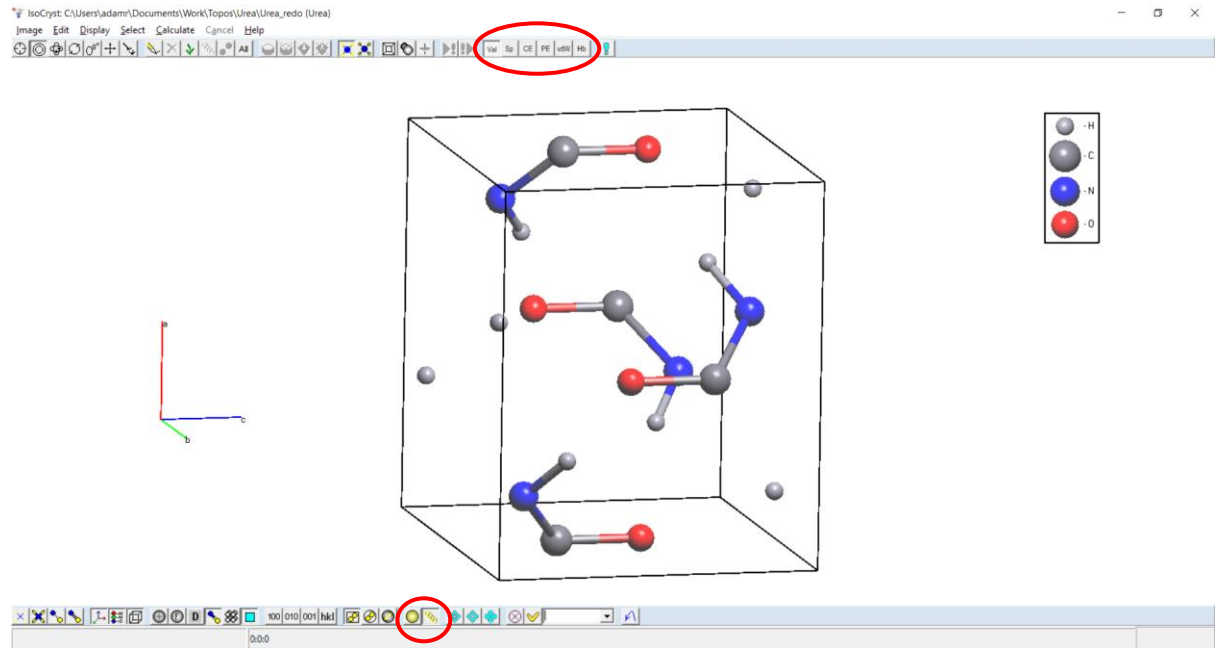
vdW and H-bonds:



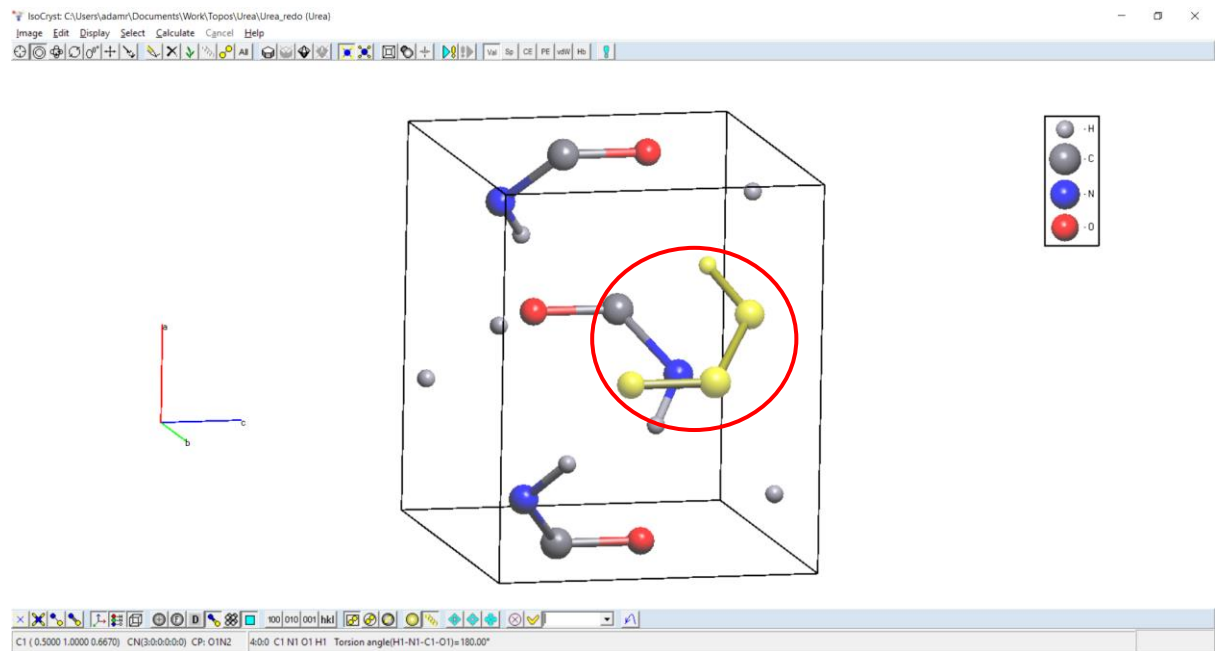
These selection methods can be combined with the grow button to grow the neighbouring molecules to a species.

Using urea as an example to produce an image of all neighbours for a central species:

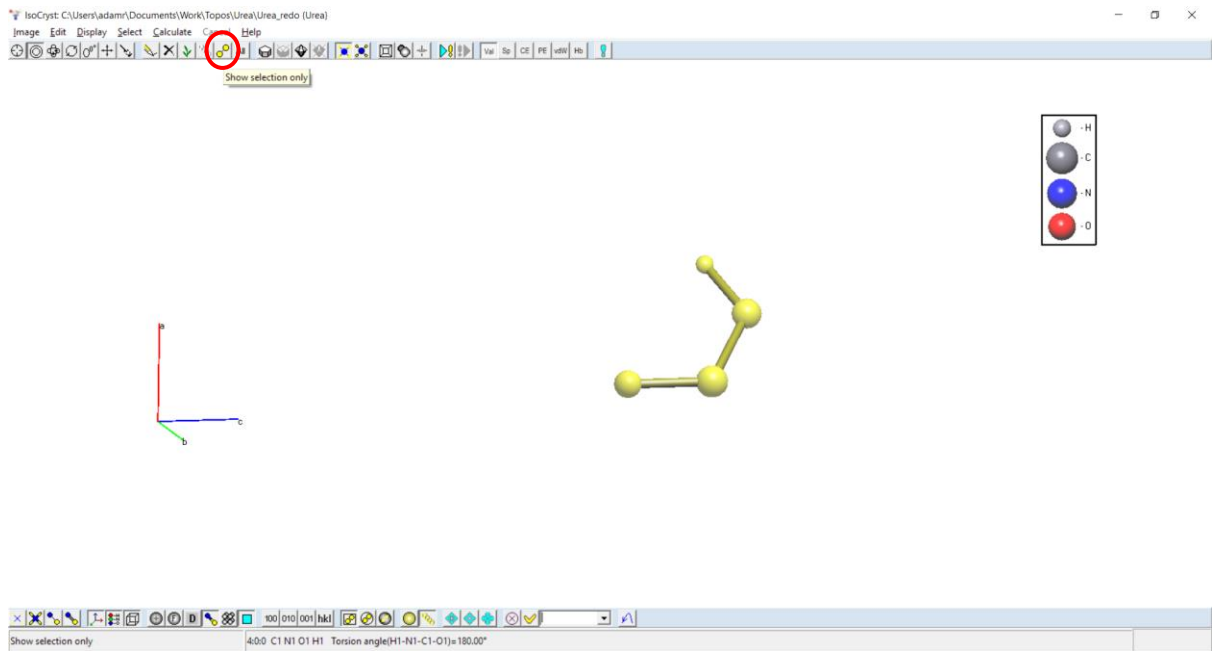
1.) Enable only valence bonds and activate Select Polymeric Chain.



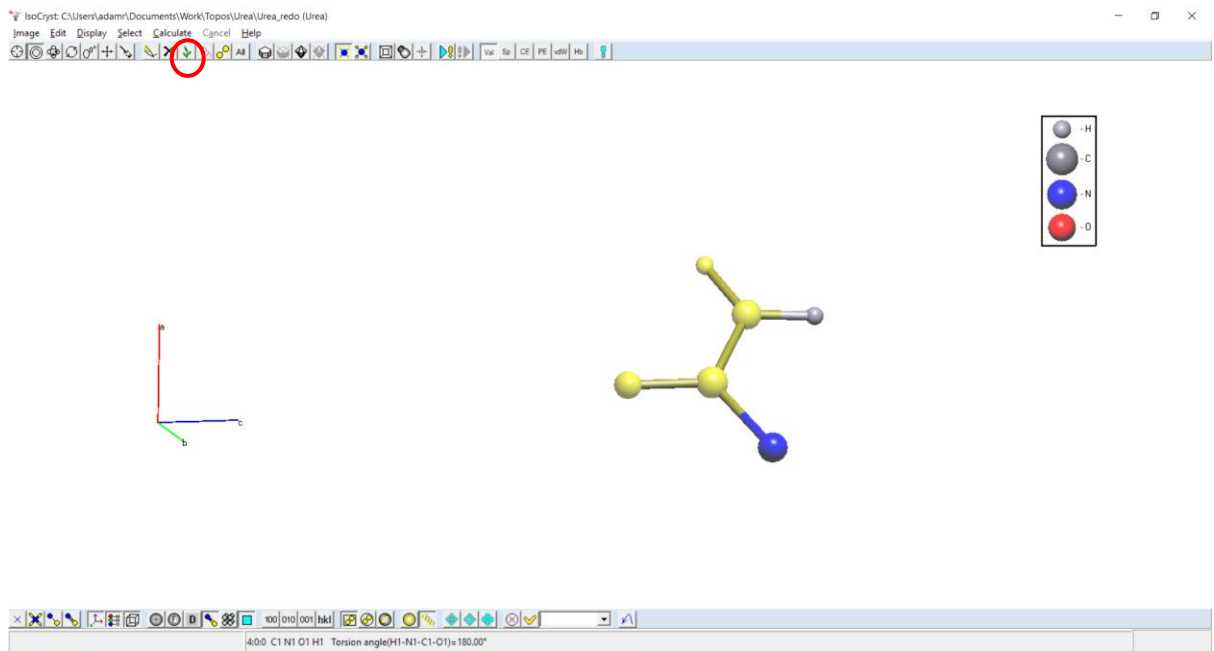
2.) Select an individual urea molecule.



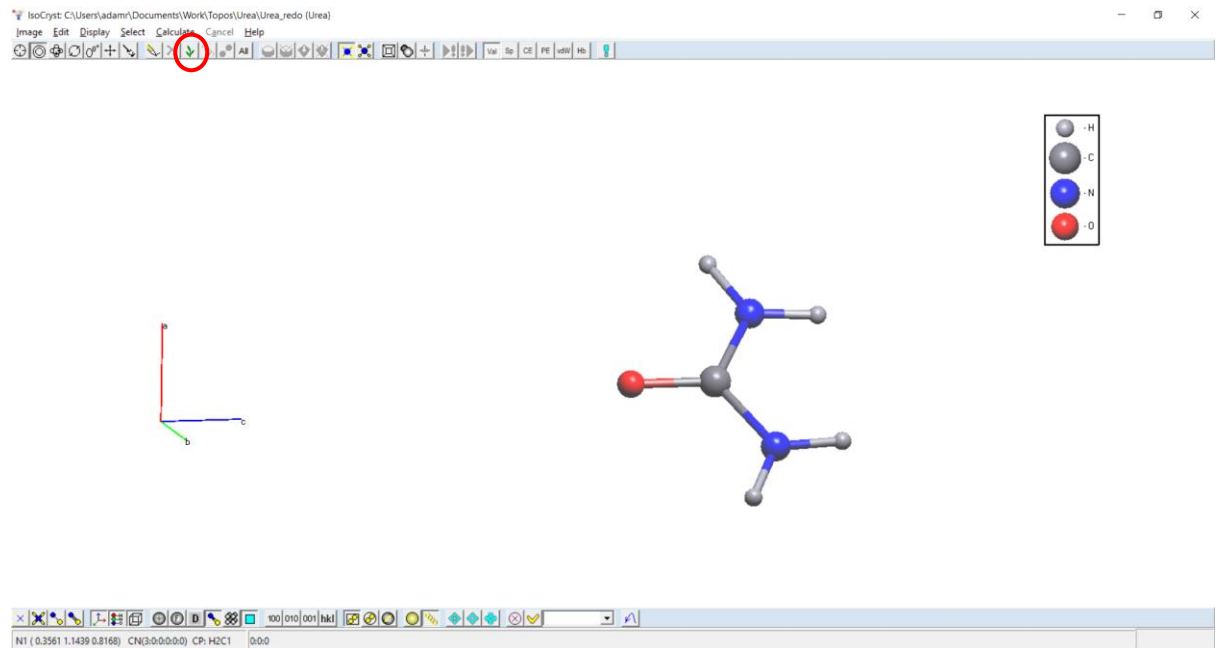
3.) Use the “show selection only” option to only display the urea molecule fragment.



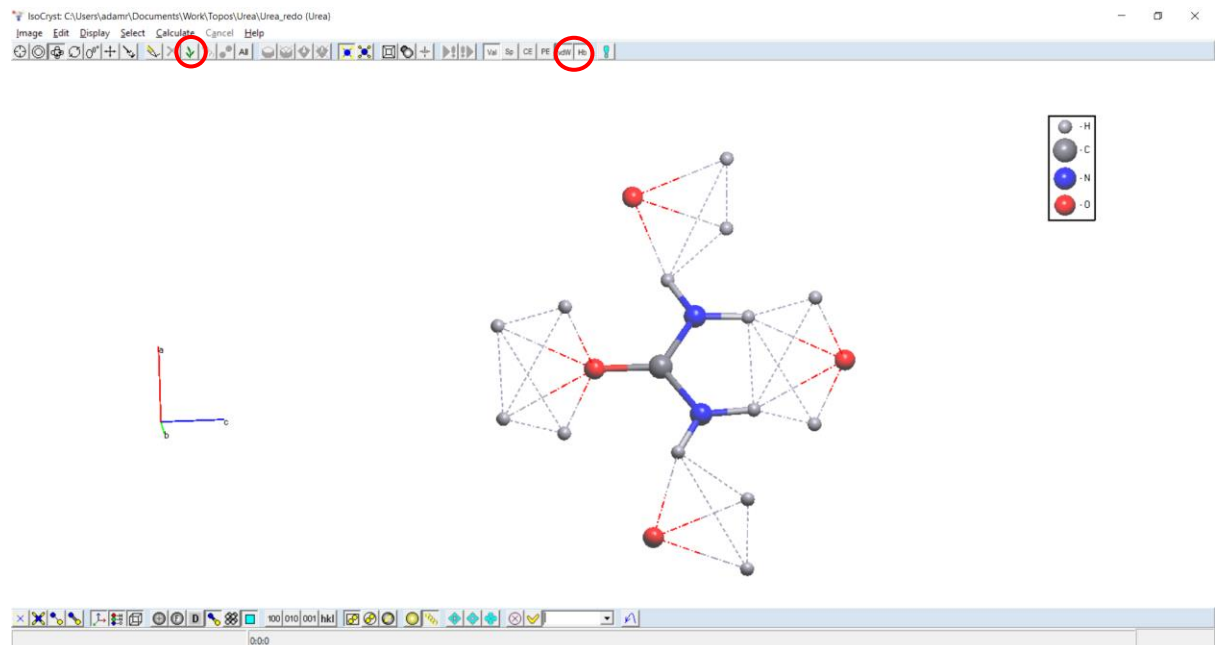
4.) Press Grow to add connected atoms to the molecule.



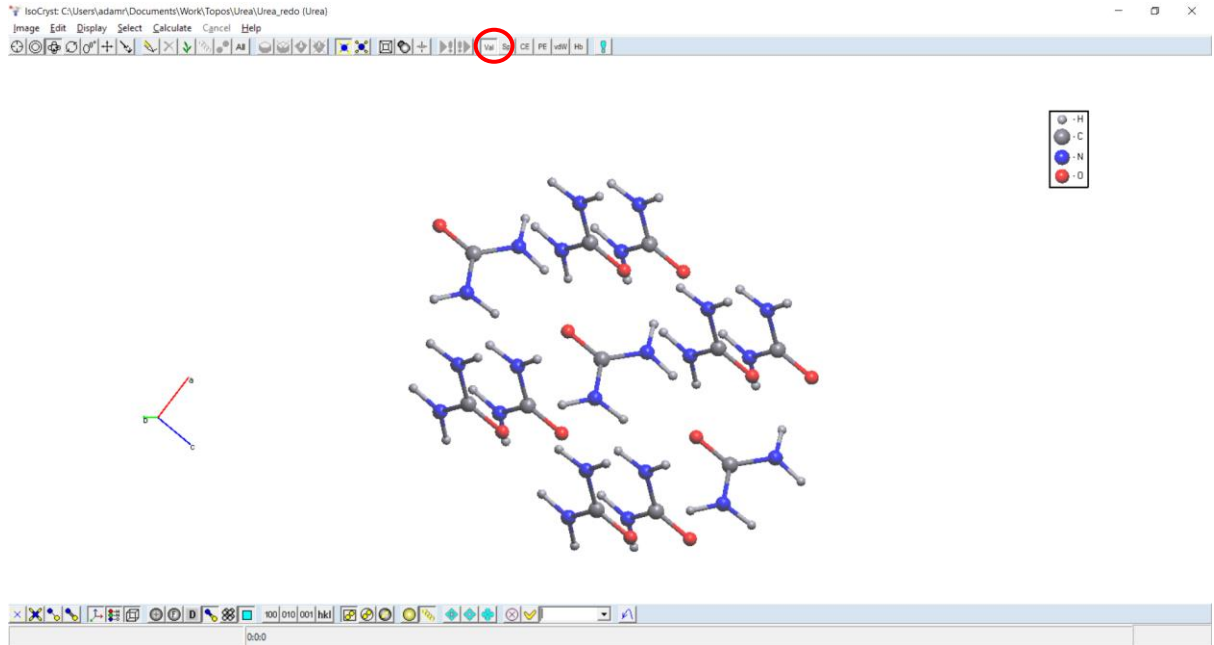
- 5.) Keep selecting the molecule and growing it until the full molecule is complete. (Right click to deselect all atoms).



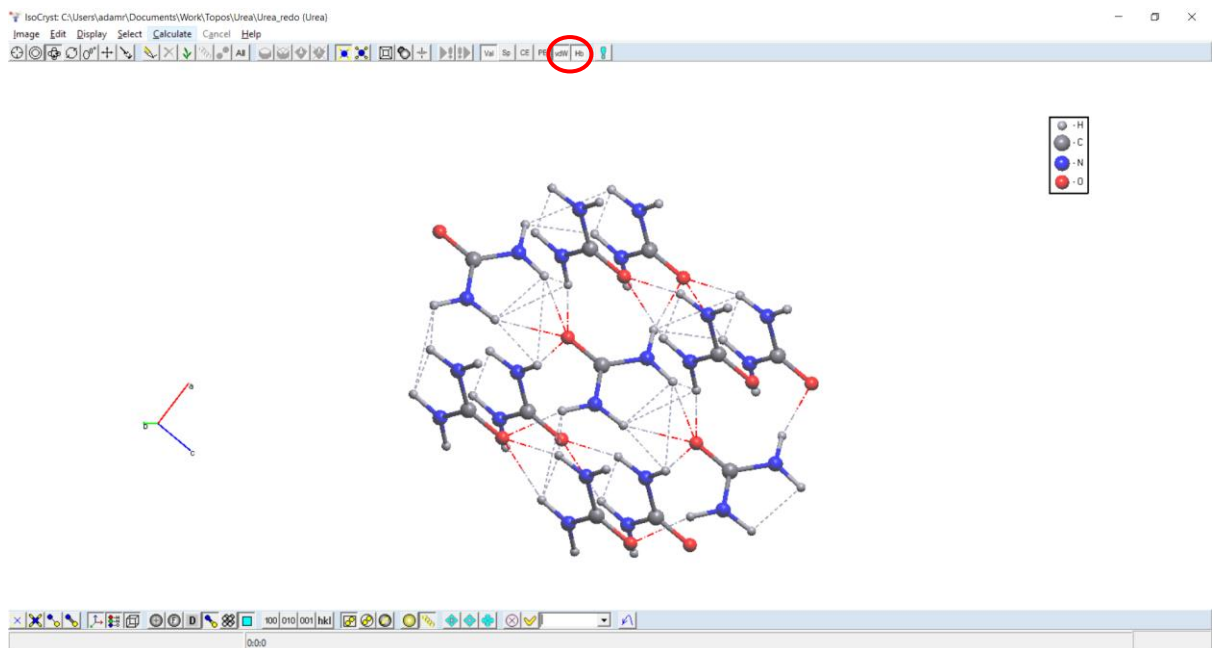
- 6.) Now activate the Hb and vdW bonds to enable growth through hydrogen bonds and vdW interactions, and press Grow once.



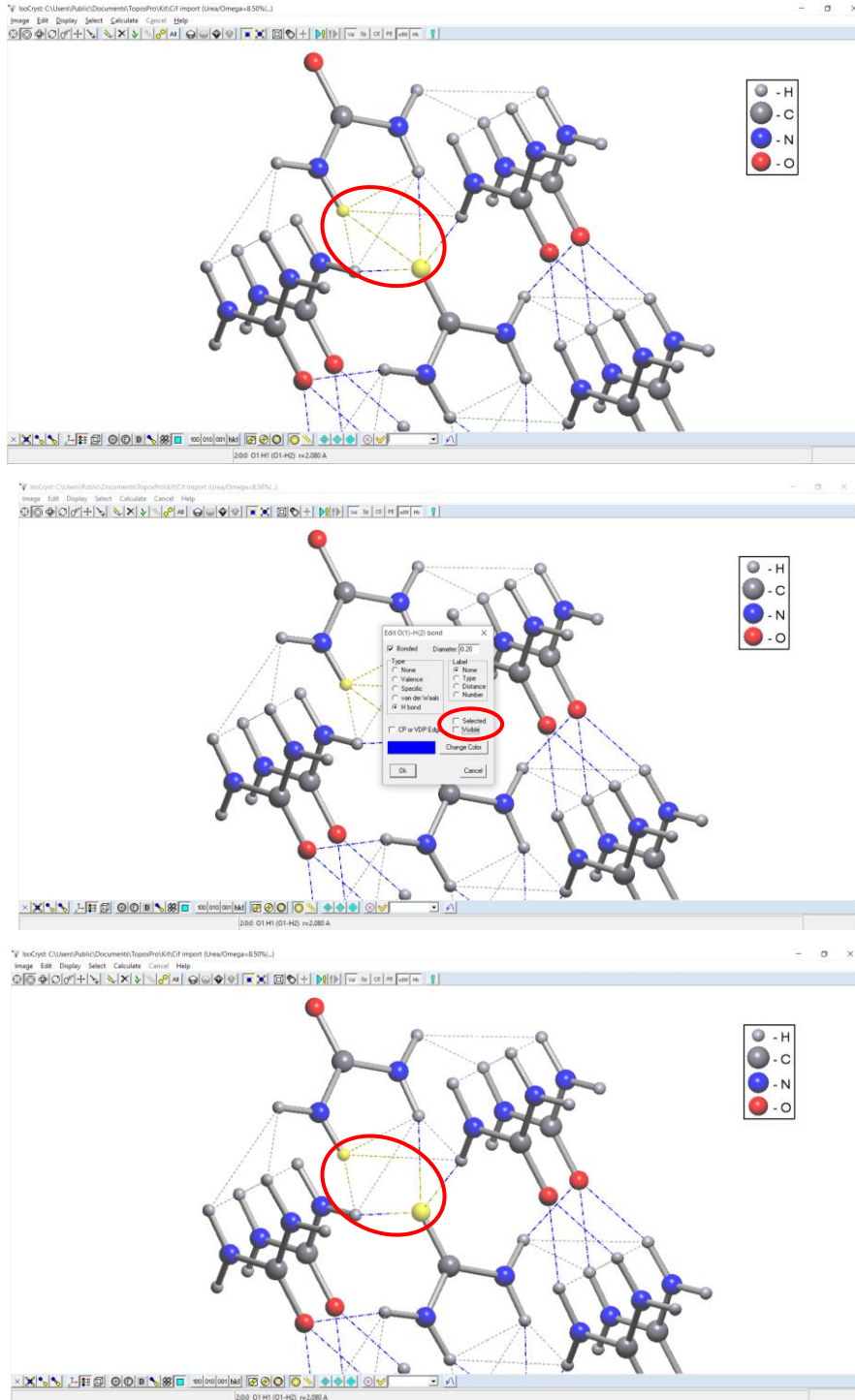
- 7.) These are the first atoms that are located on neighbouring molecules, connected to the central molecule by H-bonds and vdW interactions. Switching off Hb and vdW will return to only allowing growth via valence bonds, so the molecules will be completed if Grow is pressed repeatedly with no atoms selected.



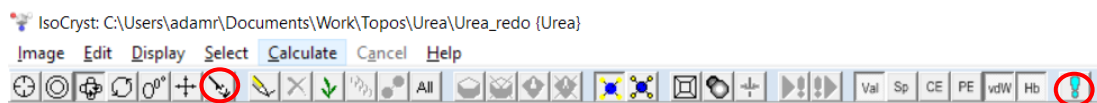
- 8.) Switch Hb and vdW back on to display the required interactions again.



Users can also change bonds individually by using the Edit Bond tool. This includes making bonds invisible, changing the drawing style and recoloring. First the bonded atoms must be selected, then Edit > Edit Bond (or **CTRL+B**), followed by selecting the options for the desired changes.



Additional options for colouring etc. can be found by clicking the exclamation mark symbol (*IsoCryst* options) or by clicking atoms with the Magic wand symbol.



Images can be saved directly from *IsoCryst* by selecting Image > Save:

