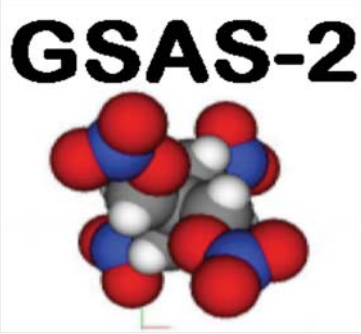
# RIGID BODIES IN GSAS-II: WHY, WHAT AND HOW

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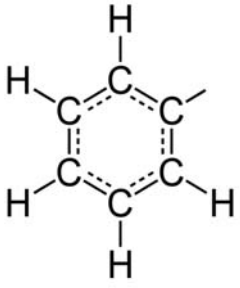
## WHY USE CONSTRAINTS?

### Reason #1. Structure refinement

Frequently, particularly with powder diffraction, one does not have enough data to independently determine the position of every non-hydrogen atom at the expected level of accuracy.

Use of constraints allows a crystallographic model to be simplified to be consistent with what has been measured.

Example: the 6 C atoms in a phenyl group ($C_6H_5$) offer 18 degrees of freedom, but if the group's internal geometry is fixed, only 6 (or less) degrees need to be treated, plus the fit structure will be more reasonable since the internal geometry of a phenyl group is well-known and does not change.



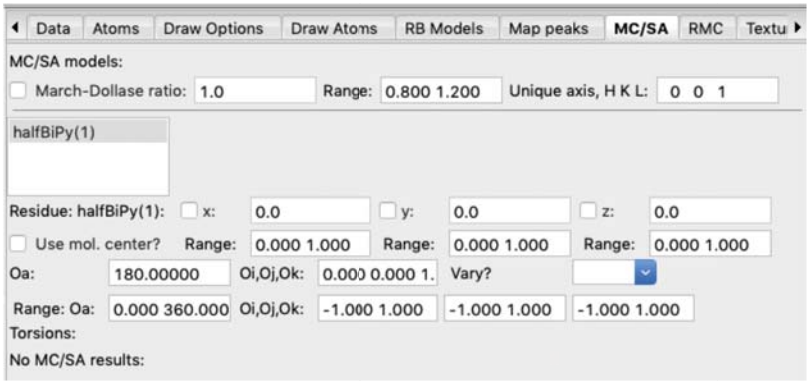
https://commons.wikimedia.org/wiki/File:Phenyl-group-2D-flat.png#/media/File:Phenyl-group-2D-flat.png

Note: when too many parameters are varied, the model will be "overfit." Unreasonable results are obtained because the data are not sufficient to independently determine all the terms that are being fit. *"Fitting to noise."*

# WHY USE RIGID BODIES?

## Reason #2. Structure solution

- When a structure must be solved, the complexity of that problem can be huge if every atom is considered as an independent entity. However, often large portions of the structure have known internal geometries and can be treated as groups where the group has only an unknown location and/or orientation. Sometimes a few torsional parameters may unknown and can also be included.
- Rigid bodies can be used with the Monte-Carlo/Simulated Annealing structure solution module (see the MC/SA tab in the Phase panel.)




# WHAT ARE RIGID BODIES?

***Rigid bodies require two sets of axes.***

1. ***the usual set of crystallographic coordinates (along a, b & c) and***
2. ***Cartesian axes, internal to the body***

***Rigid body parameters set the relation of these coordinate systems.***

- Atom positions inside rigid bodies are specified in Cartesian coordinates, relative to an origin.
- Rigid bodies will be placed inside a crystal structure with *at most* 6 degrees of freedom externally: 3 coordinates for the origin location and 3 orientation parameters. Symmetry may fix some of these.
- Group motion (TLS) terms for rigid bodies can be used generate to treat atomic displacement parameters ("thermal motion") for the atoms in the group.
- GSAS-II allows additional internal degrees of freedom in rigid bodies:
  1. **Vector rigid bodies:** offers grouped bond lengths
  2. **Residue rigid bodies:** offers torsion angles

# HOW DOES GSAS-II IMPLEMENT RIGID BODIES?

## Option 1: Vector bodies

- Vector rigid bodies have fixed geometries, but optionally allow for one or more scaling parameters
  - The scaling parameters can be refined (but can be fixed).
- The scaling parameters determine size factors for the rigid body and typically define bond lengths.
- In vector rigid body a set of atom positions ($r_j$) are generated from coordinates $v_{j,k}$

$$r_j = t_1 \cdot v_{j,1} + t_2 \cdot v_{j,2} + \ldots$$

or equivalently

$$\begin{bmatrix} \bar{r}_1 \\ \bar{r}_2 \\ \bar{r}_3 \\ . \\ . \\ . \\ \bar{r}_n \end{bmatrix} = t_1 \begin{bmatrix} \bar{v}1,1 \\ \bar{v}2,1 \\ \bar{v}3,1 \\ . \\ . \\ . \\ \bar{v}n,1 \end{bmatrix} + t_2 \begin{bmatrix} \bar{v}1,2 \\ \bar{v}2,2 \\ \bar{v}3,2 \\ . \\ . \\ . \\ \bar{v}n,2 \end{bmatrix} + \ldots$$



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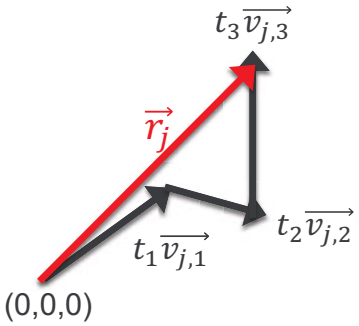
# VECTOR RIGID BODIES: CONCEPT

## A sum of vectors provides the position of each atom

- A concept that explains both the name and reasoning that helps understand how vector bodies work is to consider that each atom position is generated relative to the origin from the sum of a scaled set of vectors:

$$\vec{r_j} = t_1\vec{v_{j,1}} + t_2\vec{v_{j,2}} + t_3\vec{v_{j,3}} + \ldots$$




$$\begin{bmatrix} \bar{r}_1 \\ \bar{r}_2 \\ \bar{r}_3 \\ . \\ . \\ . \\ \bar{r}_n \end{bmatrix} = t_1 \begin{bmatrix} \bar{v}1,1 \\ \bar{v}2,1 \\ \bar{v}3,1 \\ . \\ . \\ . \\ \bar{v}n,1 \end{bmatrix} + t_2 \begin{bmatrix} \bar{v}1,2 \\ \bar{v}2,2 \\ \bar{v}3,2 \\ . \\ . \\ . \\ \bar{v}n,2 \end{bmatrix} + \ldots$$



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# FICTITIOUS VECTOR RB EXAMPLE

## Vector example: part 1A

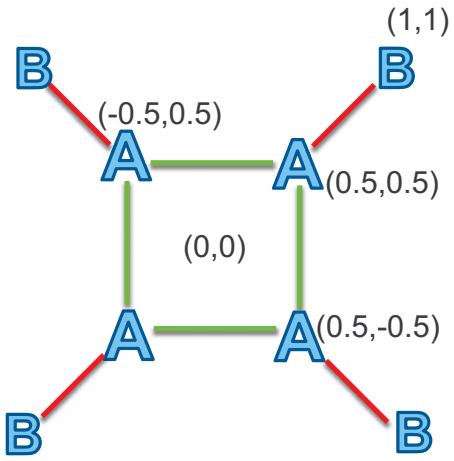
- Imagine a square rigid body with 8 atoms
  - for simplicity z (=0 for all atoms) is omitted here.

Coordinates for A:
(0.5,0.5), (0.5,-0.5), (-0.5,-0.5), (-0.5,0.5)
- A-A distance is 1

Coordinates for B:
(1,1), (1,-1), (-1,-1), (-1,1)
- A-B distance is $1/\sqrt{2}$

This can be expressed as a single matrix:

$$\begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_8 \end{pmatrix} = \begin{pmatrix} 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \\ 1 & 1 \\ -1 & 1 \\ -1 & -1 \\ 1 & -1 \end{pmatrix}$$



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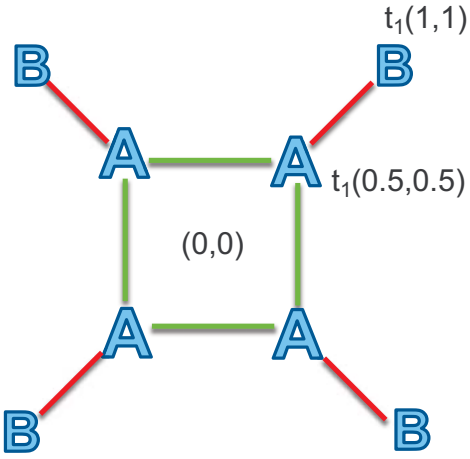
# FICTITIOUS VECTOR RB EXAMPLE

## Vector example: part 1B

- Single matrix with scaling factor :

$$\begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_8 \end{pmatrix} = t_1 \begin{pmatrix} 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \\ 1 & 1 \\ -1 & 1 \\ -1 & -1 \\ 1 & -1 \end{pmatrix}$$




Note that $t_1$ scales the entire rigid body
- A-A bonds are length $t_1$
- A-B bonds are length $t_1/\sqrt{2}$

Arbitrary units can be used for coordinates since $t_1$ scales them to Ångstroms.



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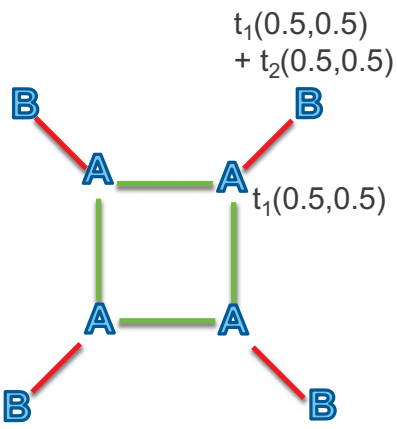
# FICTITIOUS VECTOR RB EXAMPLE

## Vector example: part 2

- With two matrices we can make A-A and A-B lengths into separate variables:

$$\begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_8 \end{pmatrix} = t_1 \begin{pmatrix} 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \\ 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \end{pmatrix} + t_2 \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \end{pmatrix}$$




Note that $t_1$ scales the entire rigid body; A & B atoms all move with $t_1$

Note that only B atoms move with $t_2$

- A-A bonds are length $t_1$
- A-B bonds are length $t_2/\sqrt{2}$



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# HOW DOES GSAS-II IMPLEMENT RIGID BODIES?

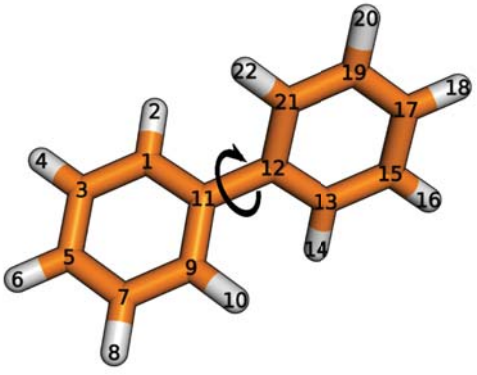
## 2. Residue rigid bodies

The dimensions of a residue rigid body cannot change, but there can be torsion angles defined, which allow sections of the molecule to reposition. There can be multiple torsions in a rigid body.

**Example**: this biphenyl [$(C_6H_5)_2$] molecule has one potential *internal* degree of freedom which is the torsional angle on the C-C bond joining the two rings (atoms 11 & 12 in diagram)

Residue coordinates must be in Ångstroms

When defining torsions, GSAS-II needs two atoms to be defined: an origin and a pivot atom. Other atoms bonded to the pivot are called riders.




Torsion origin: 11, pivot 12, riders 13 & 21 (*or equivalently, origin: 12, pivot: 11, riders: 1 & 9*)

http://erg.biophys.msu.ru/tiki/tiki-index.php?page=Ab+initio+energy+scan



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# METHODS TO GENERATE RIGID BODY COORDINATES

**There are several approaches for generating rigid body coordinates.**

1. For simple 2-D bodies, the object can sketched out on paper and the coordinates can be derived from simple geometry.
2. A molecular editor, force-field or quantum code* can be used to build and minimize the approximate (gas phase) structure for a molecule or fragment. Cartesian coordinates are then exported.
   – The open source Avogadro program is a good choice (https://sourceforge.net/projects/avogadro/); write XYZ output.
3. If you have a crystal structure (for example, from CSD) containing the rigid body you wish to use, those atoms can be extracted into a GSAS-II rigid body.
   – You can extract atoms from a structure and then optimize in Avogadro

* Note that GSAS-II will not read a Z-matrix file (which is commonly used for simulations) but OpenBabel (http://openbabel.org) will convert this to XYZ output format.





# SYMMETRY AND RIGID BODIES

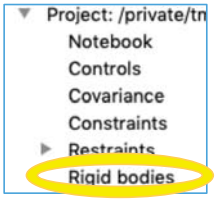
Before defining a rigid body, it is important to consider how those atoms will appear in the model. Symmetry can place constraints on the rigid body origin and axial orientation *in Cartesian space* and dictate how the RB is constructed.

- Is there internal symmetry to the rigid body? If so, is that symmetry enforced by the space group symmetry in the lattice?
  – For the example that follows, we will have a rigid body on a center of symmetry (-1) site. This means that the Cartesian origin must be placed at the crystallographic site where the -1 is located.
  – More details on symmetry and rigid bodies will be covered later
- Note that a single rigid body may be inserted in multiple locations in a single structure, but if the moiety is found in different symmetry environments, the body might need to be defined with more than one description.

If TLS parameters will be refined, it is best to put the origin at the center of mass

# HOW ARE RIGID BODIES USED IN GSAS-II?

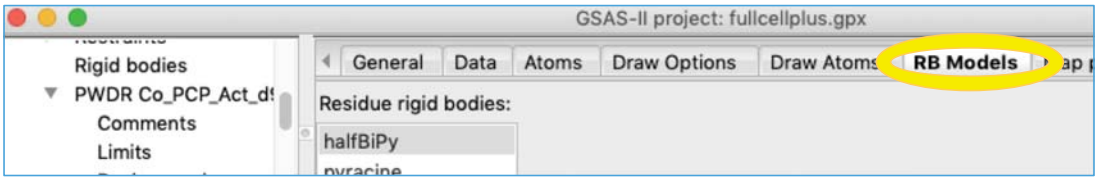
## Two steps are needed for rigid bodies




**Create:** Bodies are first defined for a project

– Define atom positions, Cartesian origin & axes. This is done in the “Rigid bodies” tree item

**Insert:** The defined rigid body is placed into a crystal structure, defining the position of the group and its orientation. Inserting a body also defines which atoms in the structure will have their coordinates generated from the body. This is done in the “RB Models” phase tab.



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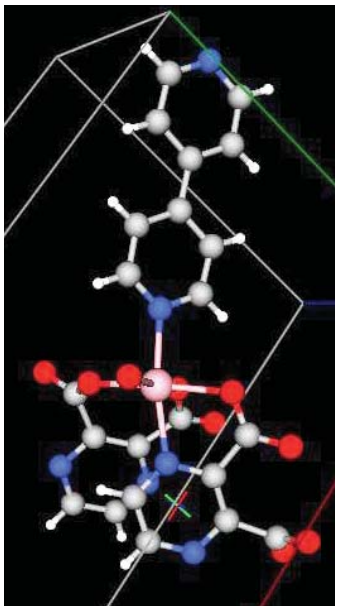
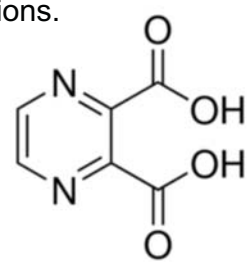
# TWO RB EXAMPLES IN ONE MOF STRUCTURE

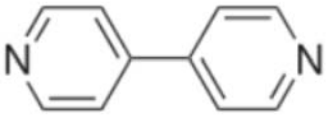
- The pictured structure is built from a metal ion, 4-4’-bipyridine molecules, and 2,3-pyrazinedicarboxylic acid ions.






2,3-pyrazinedicarboxylic acid

https://www.sigmaaldrich.com/catalog/product/aldrich/p56208?lang=en&region=US




4-4’-bipyridine

The asymmetric unit contains
- a half 4-4’-bipyridine (bipyridine)
- a single complete 2,3-pyrazinedicarboxylic acid ion (pyrazine)

The symmetry of each needs to be considered separately



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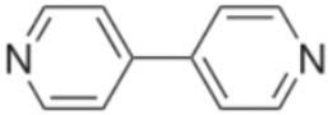
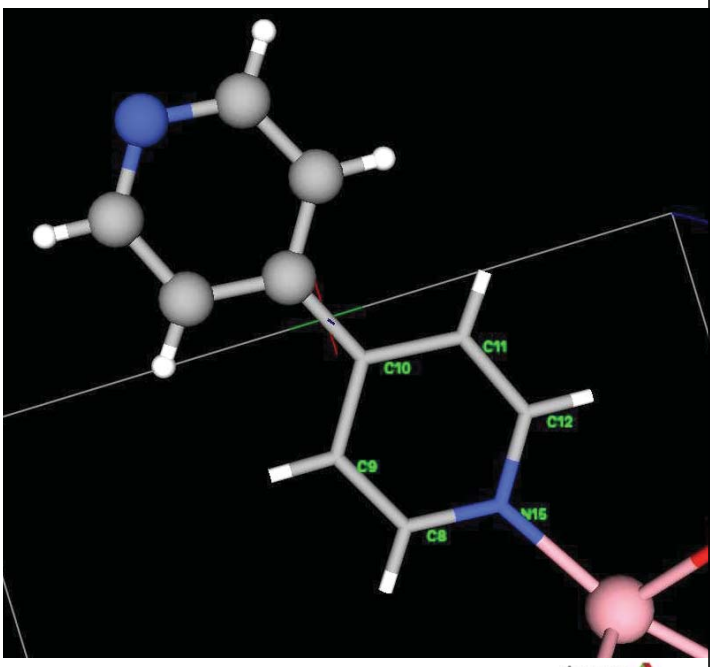
# 4-4'-BIPYRIDINE (BIPYRIDINE)




## Care required: this is on a special position

- The asymmetric unit is drawn as stick figure & labeled (symmetry-generated atoms are ball-and-stick)
- Note that there is a center of symmetry ($\bar{1}$) between C10 and its symmetry-twin.
- Examination of plot or coordinates identifies the $\bar{1}$ location as $(0,\frac{1}{2},1)$

To preserve the symmetry, the origin for the rigid body must be at the midpoint between C10 and C10'. That will be placed at $(0,\frac{1}{2},1)$ in crystal coordinates.



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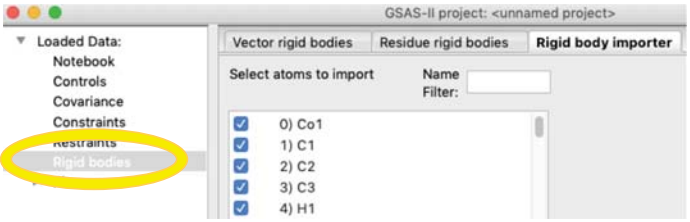
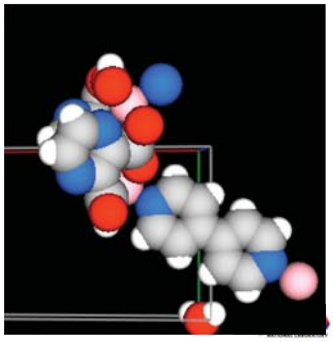
# CREATE THE BIPYRIDINE RIGID BODY (1)

## Work can be done in a new project, but a phase is needed to create the "Rigid Bodies" tree entry

In this example we will use a publication as the source of coordinates for the rigid body.

- Note that because we will need both C10 and C10' to establish the origin, the structure must be expanded to provide both atoms before it is read in.
- From either "Vector rigid bodies" or "Residue rigid bodies" use the Edit Vector Body/Extract from file menu command
- Select a file format, in this case CIF and then find the CIF file and select it
  - All atoms are brought into the "Rigid body importer" selector and are plotted.

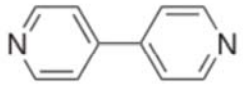


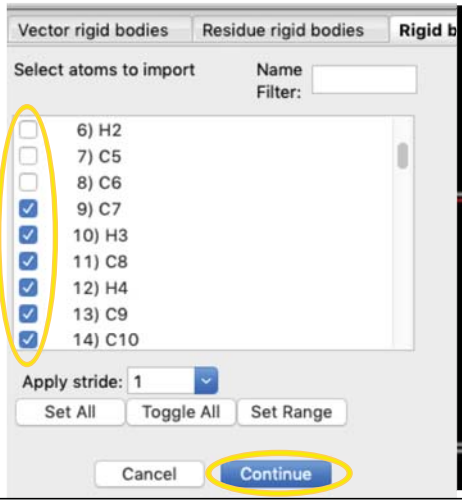



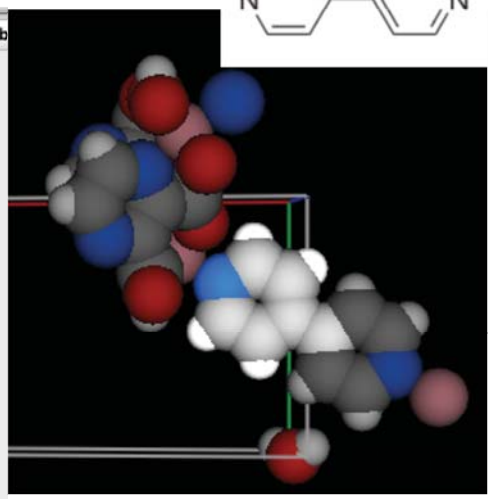
# CREATE THE BIPYRIDINE RIGID BODY (2)

## Select the atoms needed to build the rigid body

- In the Atom selector, unselect all atoms, and select only the atoms from one ring plus one atom on the other ring.
  - Note that selected atoms are brightly colored while unselected atoms appear much darker.
- Press continue



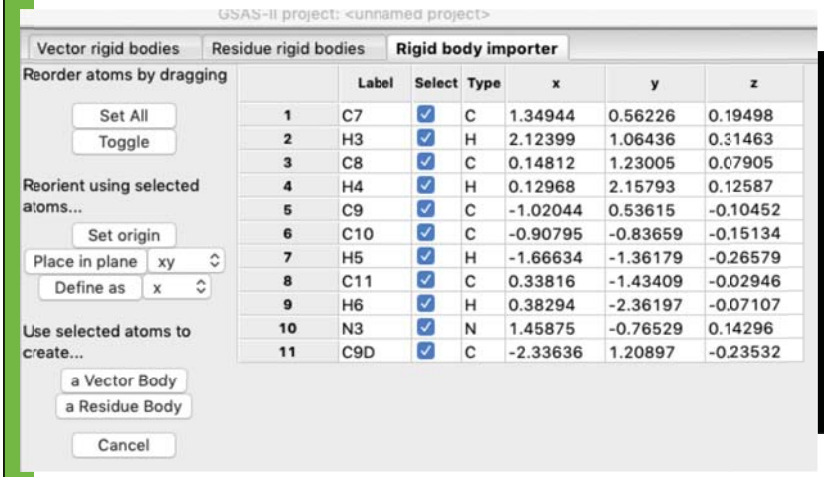



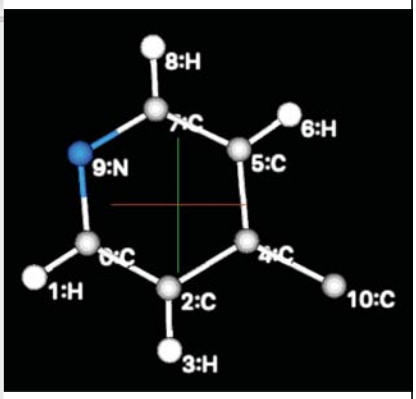
# CREATE THE BIPYRIDINE RIGID BODY (3)

## For convenience (but not required) we will define the axes orientation

Once the atoms are selected, a new table with Cartesian coordinates and a plot of the atoms is shown.




| | Label | Select | Type | x | y | z |
|---|---|---|---|---|---|---|
| 1 | C7 | ☑ | C | 1.34944 | 0.56226 | 0.19498 |
| 2 | H3 | ☑ | H | 2.12399 | 1.06436 | 0.31463 |
| 3 | C8 | ☑ | C | 0.14812 | 1.23005 | 0.07905 |
| 4 | H4 | ☑ | H | 0.12968 | 2.15793 | 0.12587 |
| 5 | C9 | ☑ | C | -1.02044 | 0.53615 | -0.10452 |
| 6 | C10 | ☑ | C | -0.90795 | -0.83659 | -0.15134 |
| 7 | H5 | ☑ | H | -1.66634 | -1.36179 | -0.26579 |
| 8 | C11 | ☑ | C | 0.33816 | -1.43409 | -0.02946 |
| 9 | H6 | ☑ | H | 0.38294 | -2.36197 | -0.07107 |
| 10 | N3 | ☑ | N | 1.45875 | -0.76529 | 0.14296 |
| 11 | C9D | ☑ | C | -2.33636 | 1.20897 | -0.23532 |



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# CREATE THE BIPYRIDINE RIGID BODY (4)

## Put atoms in plane (optional)

With all atoms selected, click on the place in plane, with “xy” selected adjacent. Note that the z values are nearly zero. There is no visible change in the plot except that the cross hairs rotate, showing the different axes directions.

Reorder atoms by dragging

Set All

Toggle

Reorient using selected atoms...

Set origin

Place in plane xy

Define as x

Use selected atoms to create...

a Vector Body

a Residue Body

Cancel

| | Label | Select | Type | x | y | z |
|---|---|---|---|---|---|---|
| 1 | C7 | ☑ | C | 1.35977 | 0.57110 | 0.19498 |
| 2 | H3 | ☑ | H | 2.14013 | 1.07844 | 0.31463 |
| 3 | C8 | ☑ | C | 0.14933 | 1.23245 | 0.07905 |
| 4 | H4 | ☑ | H | 0.13121 | 2.16151 | 0.12587 |
| 5 | C9 | ☑ | C | -1.02875 | 0.53042 | -0.10452 |
| 6 | C10 | ☑ | C | -0.91462 | -0.84298 | -0.15134 |
| 7 | H5 | ☑ | H | -1.67817 | -1.37313 | -0.26579 |
| 8 | C11 | ☑ | C | 0.34058 | -1.43382 | -0.02946 |
| 9 | H6 | ☑ | H | 0.38547 | -2.36262 | -0.07107 |
| 10 | N3 | ☑ | N | 1.46983 | -0.75741 | 0.14296 |
| 11 | C9D | ☑ | C | -2.35478 | 1.19605 | -0.23532 |



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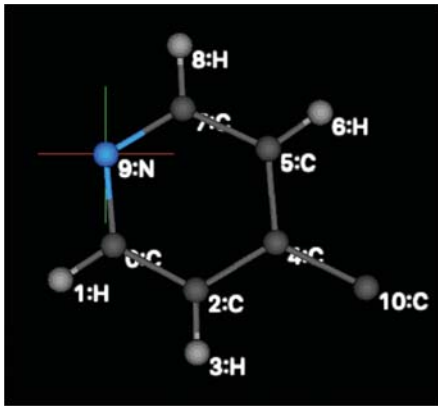
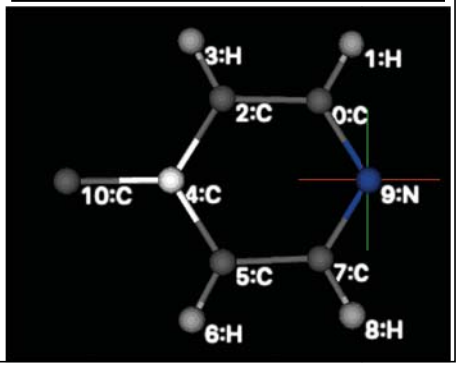
# CREATE THE BIPYRIDINE RIGID BODY (5)

## Set up the axes (optional)




We will make the x-axis run from the N atom to one of the C atoms by unselecting the N atom and then toggle (so that it is the only selected atom). Temporarily make that atom the origin by pressing the “Set origin” button. Note that the cross hairs move to the N atom and its coordinates are now (0,0,0).

Then unselect the N atom and select the C atom and press ”define as” with “x” selected. The body rotates and the selected C atom is now at (x,0,0)




Reorder atoms by dragging

Set All

Toggle

Reorient using selected atoms...

Set origin

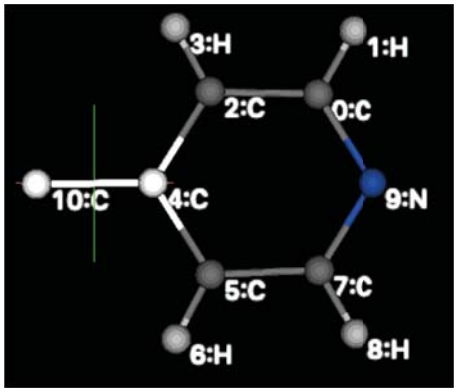
Place in plane xy

Define as x

| | Label | Select | Type | x | y | z |
|---|---|---|---|---|---|---|
| 1 | C7 | ☐ | C | 0.70648 | -1.13046 | 0.00170 |
| 2 | H3 | ☐ | H | 0.24528 | -1.93893 | 0.00025 |
| 3 | C8 | ☐ | C | 2.08541 | -1.16375 | 0.00387 |
| 4 | H4 | ☐ | H | 2.52715 | -1.98126 | 0.00823 |
| 5 | C9 | ☑ | C | 2.81094 | 0.00000 | -0.00000 |
| 6 | C10 | ☐ | C | 2.08028 | 1.16849 | 0.00522 |
| 7 | H5 | ☐ | H | 2.51608 | 1.98954 | 0.01093 |
| 8 | C11 | ☐ | C | 0.69387 | 1.11861 | 0.00003 |
| 9 | H6 | ☐ | H | 0.22844 | 1.92363 | -0.00244 |
| 10 | N3 | ☐ | N | 0.00000 | 0.00000 | 0.00000 |
| 11 | C9D | ☐ | C | 4.29458 | 0.01585 | 0.00141 |

# CREATE THE BIPYRIDINE RIGID BODY (6)

## Required: place origin on center of symmetry




The midpoint between the two rings *must* be the location of the center of symmetry.

Select the two C atoms that join the two rings. Then press the “Set origin” button to put the origin at the average of the two selected positions.

Reorder atoms by dragging

Set All | Toggle

Reorient using selected atoms...

Set origin

Place in plane xy

Define as x

Use selected atoms to create...

a Vector Body

| | Label | Select | Type | x | y | z |
|---|---|---|---|---|---|---|
| 1 | C7 | ☐ | C | -2.84628 | -1.13838 | 0.00099 |
| 2 | H3 | ☐ | H | -3.30748 | -1.94686 | -0.00046 |
| 3 | C8 | ☐ | C | -1.46735 | -1.17167 | 0.00316 |
| 4 | H4 | ☐ | H | -1.02561 | -1.98919 | 0.00753 |
| 5 | C9 | ☑ | C | -0.74182 | -0.00793 | -0.00071 |
| 6 | C10 | ☐ | C | -1.47248 | 1.16056 | 0.00452 |
| 7 | H5 | ☐ | H | -1.03668 | 1.98162 | 0.01023 |
| 8 | C11 | ☐ | C | -2.85889 | 1.11068 | -0.00067 |
| 9 | H6 | ☐ | H | -3.32432 | 1.91571 | -0.00315 |
| 10 | N3 | ☐ | N | -3.55276 | -0.00793 | -0.00071 |
| 11 | C9D | ☑ | C | 0.74182 | 0.00793 | 0.00071 |

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# CREATE THE BIPYRIDINE RIGID BODY (7)

Set origin

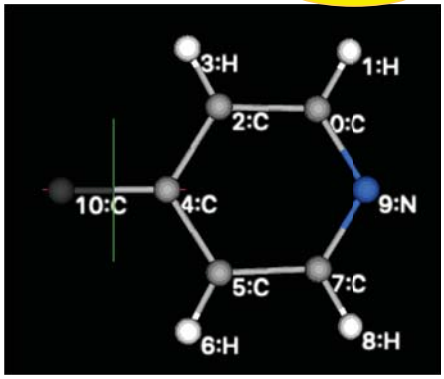
Place in plane xy

Define as x

Use selected atoms to create...

a Vector Body

## Export all atoms in the ring, but not the “extra” atom




We want to export all but the last C atom (C11). (This can be done simply by unselect the 4th atom and press toggle, highlighting all atoms in the one ring.)

Then create a residue rigid body by pressing the “a Residue Body” button.

Change the name of the body

If you will use the body in a different project, use “Edit Rigid Body”/“Save rigid body” to write a file.

Note: while we will use a residue body here, since there are no torsions for this body, a vector rigid body would work just as well.

Vector rigid bodies | Residue rigid bodies

Residue name: half-bipy | Plot | Delete | Strip H-atoms

Orientation reference non-H atoms A-B-C: C7 | H3 | C8

| | Name | Type | Cart x | Cart y | Cart z |
|---|---|---|---|---|---|
| 0 | C7 | C | -2.84628 | -1.13838 | 0.00099 |
| 1 | H3 | H | -3.30748 | -1.94686 | -0.00046 |
| 2 | C8 | C | -1.46735 | -1.17167 | 0.00316 |
| 3 | H4 | H | -1.02561 | -1.98919 | 0.00753 |
| 4 | C9 | C | -0.74182 | -0.00793 | -0.00071 |
| 5 | C10 | C | -1.47248 | 1.16056 | 0.00452 |
| 6 | H5 | H | -1.03668 | 1.98162 | 0.01023 |
| 7 | C11 | C | -2.85889 | 1.11068 | -0.00067 |
| 8 | H6 | H | -3.32432 | 1.91571 | -0.00315 |
| 9 | N3 | N | -3.55276 | -0.00793 | -0.00071 |

# INSERT THE 2,3-PYRAZINEDICARBOXYLIC ACID (PYRAZINE)

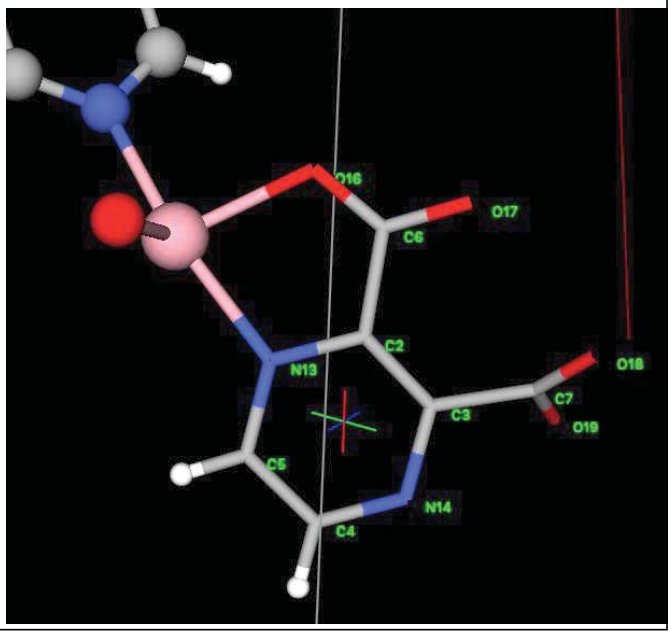

## Note: not on a special position

The asymmetric unit structure has been drawn here

- Pyrazine asymmetric unit drawn as stick figure & labeled

- Note that the ion is planar with the exception of the 4 oxygens
  - The O atoms will need torsions to position them

There is no internal symmetry here so the origin of the body can be arbitrary

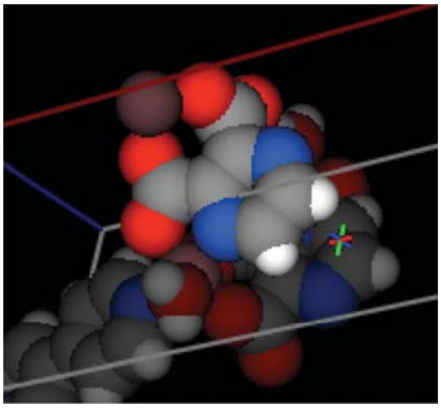


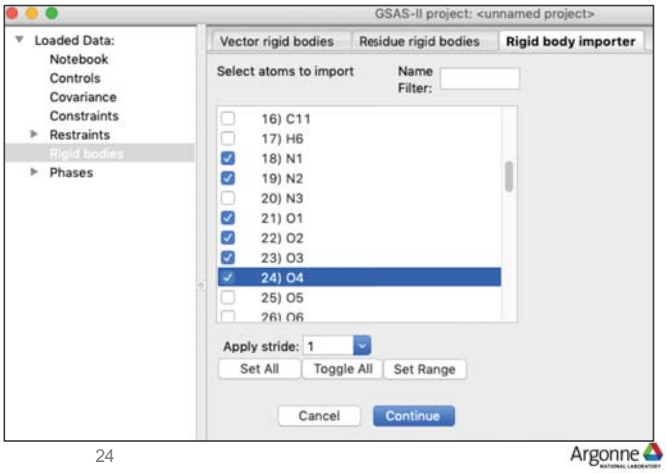

# CREATE THE PYRAZINE RIGID BODY (1)

## Import the CIF file again, but select different atoms

Repeating the previous process: use “Edit Vector Body”/“Extract from file” menu command again

- Select a file format (in this case CIF) and then find the CIF file and select it. Then select the 6 C atoms, 2 N and 2 H atoms and 4 O atoms in the pyrazine ion.
  - To see, it will help to reorient the 3D display by dragging with the mouse left and right buttons





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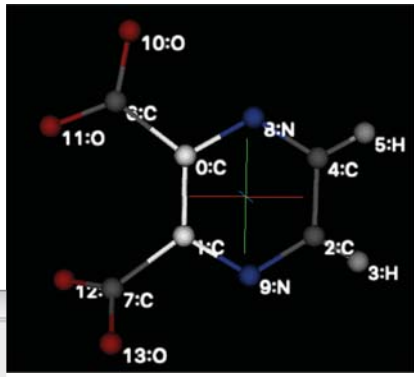
# CREATE THE PYRAZINE RIGID BODY (2)

## Place atoms in a plane and redefine the origin

Unselect the O atoms, since they are not planar and press “Set origin” and “Place in plane” buttons (with “xy” selected)

Select the two C atoms and press “Define as” (with “x” selected) to place the x-axis between the selected atoms




Vector rigid bodies | Residue rigid bodies | **Rigid body importer**

Reorder atoms by dragging

Set All | Toggle

Reorient using selected atoms...

Set origin

Place in plane xy | Define as x

Use selected atoms to create...

a Vector Body | a Residue Body

Cancel

| | Label | Select | Type | x | y | z |
|---|---|---|---|---|---|---|
| 1 | C1 | ☑ | C | 1.06807 | -0.69414 | -0.00846 |
| 2 | C2 | ☑ | C | 1.07052 | 0.69414 | 0.00846 |
| 3 | C3 | ☐ | C | -1.21613 | 0.68002 | -0.01733 |
| 4 | H1 | ☐ | H | -2.02415 | 1.13756 | -0.08688 |
| 5 | C4 | ☐ | C | -1.23793 | -0.69157 | 0.03080 |
| 6 | H2 | ☐ | H | -2.05011 | -1.14387 | 0.03336 |
| 7 | C5 | ☐ | C | 2.27923 | -1.61033 | -0.10121 |
| 8 | C6 | ☐ | C | 2.29003 | 1.62459 | 0.03609 |
| 9 | N1 | ☐ | N | -0.08963 | -1.37842 | 0.07570 |
| 10 | N2 | ☐ | N | -0.08990 | 1.38202 | 0.02947 |
| 11 | O1 | ☐ | O | 2.07147 | -2.82652 | 0.12454 |
| 12 | O2 | ☐ | O | 3.38051 | -1.14177 | -0.43040 |
| 13 | O3 | ☐ | O | 3.09571 | 1.61361 | -0.92593 |
| 14 | O4 | ☐ | O | 2.34487 | 2.42287 | 0.98654 |

Note that these origin & axes settings are for convenience in viewing and understanding the body, but are not required.

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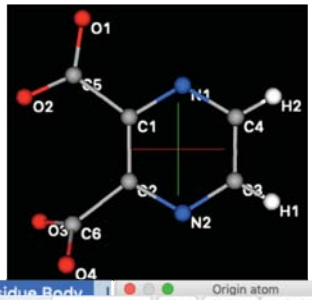
# CREATE THE PYRAZINE RIGID BODY (3)

## Create body & define carboxylic torsions

Since this ion needs torsional rotation for the carboxylic groups, a residue rigid body is required.

- Select all atoms and then press “a Rigid Body” to create it.
- Select the new body and rename it.
- Define two torsional degrees of freedom: (It helps to press the “Plot” button to identify the atoms.) Use Edit Rigid Body/Define torsion menu item.
  - Origin C1; Pivot C5 (riding O1 & O2)
  - Origin C2; Pivot C6 (riding O3 & O4)

Save the rigid body, if will be needed in a different project.




Edit Residue Body — Origin atom

Residue name: pyrazine | Plot | Delete | Strip H-atoms

Orientation reference non-H atoms A-B-C: C1 | C2

| | Name | Type | Cart x | Cart y | Cart z |
|---|---|---|---|---|---|
| 0 | C1 | C | 1.06807 | -0.69414 | -0.00846 |
| 1 | C2 | C | 1.07052 | 0.69414 | 0.00846 |
| 2 | C3 | C | -1.21613 | 0.68002 | -0.01733 |
| 3 | H1 | H | -2.02415 | 1.13756 | -0.08688 |
| 4 | C4 | C | -1.23793 | -0.69157 | 0.03080 |
| 5 | H2 | H | -2.05011 | -1.14387 | 0.03336 |
| 6 | C5 | C | 2.27923 | -1.61033 | -0.10121 |
| 7 | C6 | C | 2.29003 | 1.62459 | 0.03609 |
| 8 | N1 | N | -0.08963 | -1.37842 | 0.07570 |
| 9 | N2 | N | -0.08990 | 1.38202 | 0.02947 |
| 10 | O1 | O | 2.07147 | -2.82652 | 0.12454 |
| 11 | O2 | O | 3.38051 | -1.14177 | -0.43040 |
| 12 | O3 | O | 3.09571 | 1.61361 | -0.92593 |
| 13 | O4 | O | 2.34487 | 2.42287 | 0.98654 |

| Sel | | Bond | Angle | Riding atoms |
|---|---|---|---|---|
| ◉ | Del | C1 C5 | 0.00 | O1, O2 |
| ○ | Del | C2 C6 | 0.00 | O3, O4 |

Selected torsion angle:

# PREPARE TO INSERT RIGID BODIES

In this case we have a rough idea where the rigid bodies are located, so we will place them to match approximate of atoms in the structure.

Notes

- The rigid bodies have H atoms, but the atoms list does not; any rigid body atoms not in the atoms list can be added to the atoms list when the body is inserted
- There are some distortions in groups that will be corrected when atom positions are generated by from the rigid bodies.
- Note the atom list need not be ordered to match the rigid body, but that can make things more convenient.



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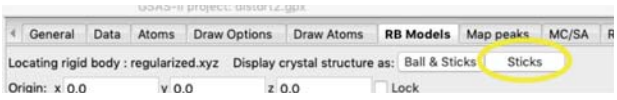
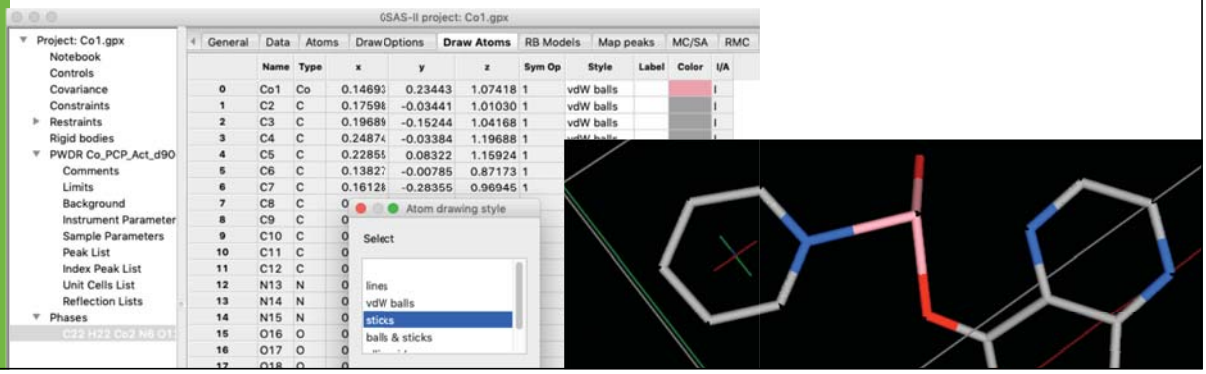
# VIEWING STRUCTURES & RIGID BODIES

The view of the structure is determined by the atoms copied from the asymmetric cell into the Draw Atoms array and their settings.

- To best view the structure and rigid body use “Stick” or “Balls & Stick” modes.
  - Select using the buttons on the RB Models tab or by double-clicking on the column labeled ”style” in the “Draw Atoms” tab



# ORIENTING STRUCTURES IN WINDOW

## Mouse movements change view of structure

When the structure is viewed, use of the mouse buttons changes the view of the crystal structure:

- Holding down left button (left drag): rotates axes around screen x & y
- Holding down right button (right drag): Moves the viewpoint, which is kept at the center of the screen (effectively translating the structure)
- Holding down center button (center drag): rotates axes around screen z
- Rotating the scroll wheel: changes “camera position” (zoom in/out)

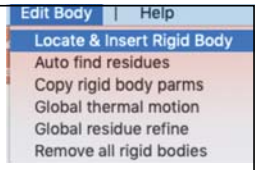
*When the Rigid Body and structure are shown together, holding the Alt button while dragging the mouse causes the same movements, but only to the rigid body*

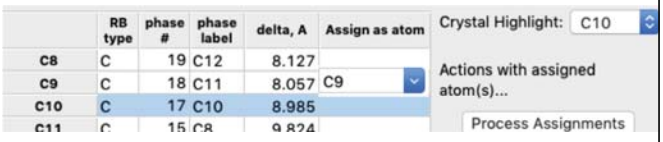
- Pressing the “c” key sets the viewpoint to (½,½,½) [value can also be edited in Draw Options tab]





# HIGHLIGHTING ATOMS



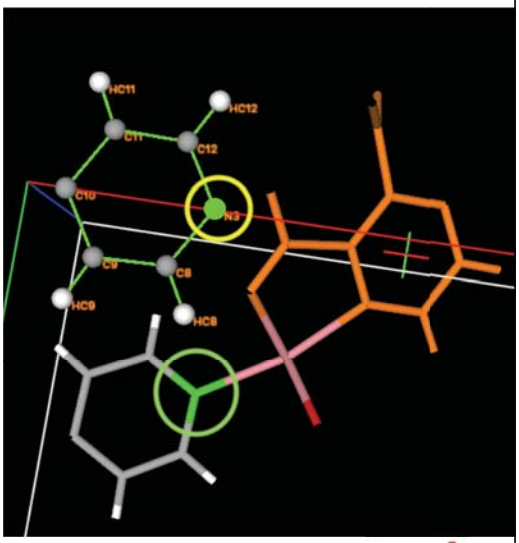




The “Locate and Insert Rigid Body” command creates table with rigid body atoms and matching atoms in crystal structure (with the distance between them).

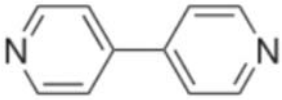
Atoms can be paired.

To help determine which atoms should be paired, specific atoms can be highlighted.

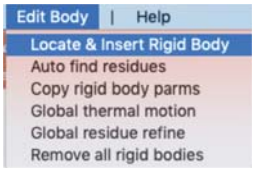
- Selecting a row causes the rigid body atom and the matching crystal structure atom to be highlighted
- To highlight a different atom in the crystal, use the “Crystal Highlight” pulldown, or press Tab to select crystal atoms
- Pressing Alt+Tab cycles through the rigid body atoms.



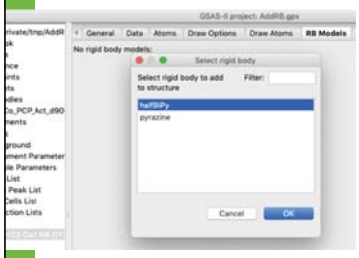
# INSERT THE BIPYRIDINE INTO THE STRUCTURE (1)

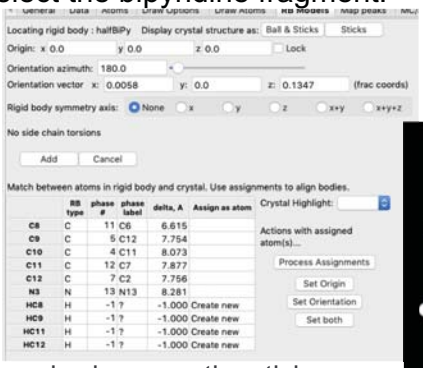


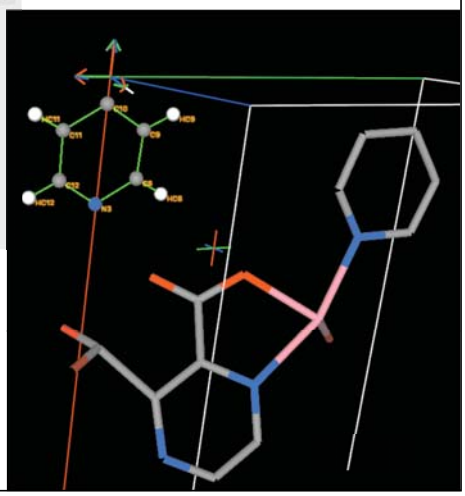

## Assumes rigid body is already defined (or read in)




- Go to RB Models phase tab; use “Edit Body”/“Locate and Insert Rigid Body”; select the bipyridine fragment.



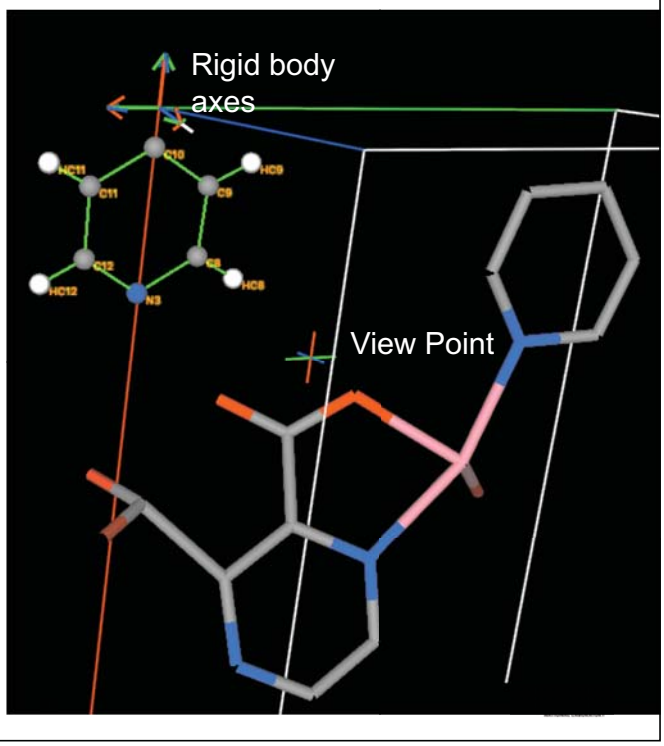
Note that the crystal structure is shown as the stick diagram; the rigid body is shown as balls & green sticks

Also, the rigid body has H atoms, the crystal structure does not; H atoms will be added to structure (noted as “Create new” in table) since they can’t be matched



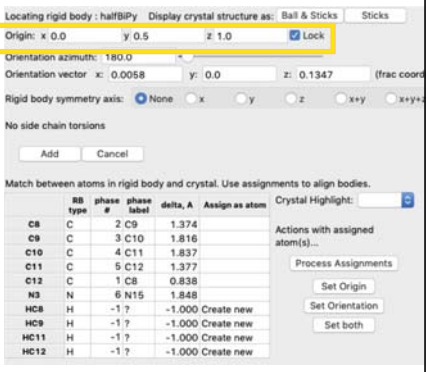
# WHAT IS SHOWN IN STRUCTURE PLOT

- The View Point (six-line star) shows the cell axes. Move with right mouse; reset to (½,½,½) with “c”
- The triplet with arrows shows the Cartesian axes with the origin placed the rigid body position
- Axes & cell edges are colored red, green & blue for x, y & z, respectively
- The white line in the triplet is the vector direction for the rigid body orientation. The azimuth angle rotates the rigid body around this axis.

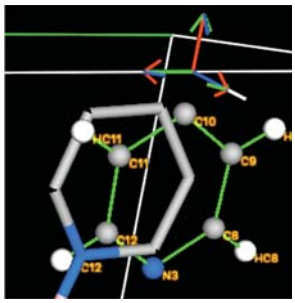


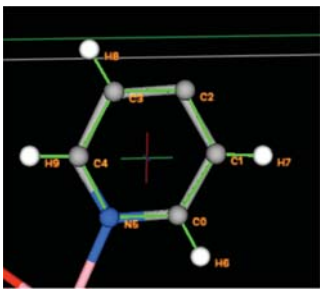
# INSERT THE BIPYRIDINE INTO THE STRUCTURE (2)

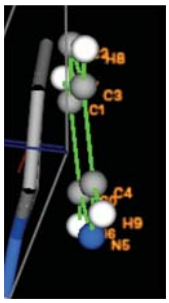
## Position RB close to location in structure

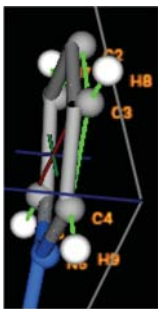



- Use mouse to reorient view of structure
- Holding Alt down & use of Left/Middle/Right repositions the rigid body.
- As noted before: bipyradine origin must be at $\bar{1}$
- Edit origin to enter $(0,\frac{1}{2},1)$ (N.B. RB is now close as shown below)
  - Press lock to prevent changing this by accident with Alt+right mouse
- Use Alt+Left & Alt+Middle to get bodies close; rotating plot for multiple views




Note that as the atoms are moved, the table is updated with the closest matches between atoms and the distances between them.



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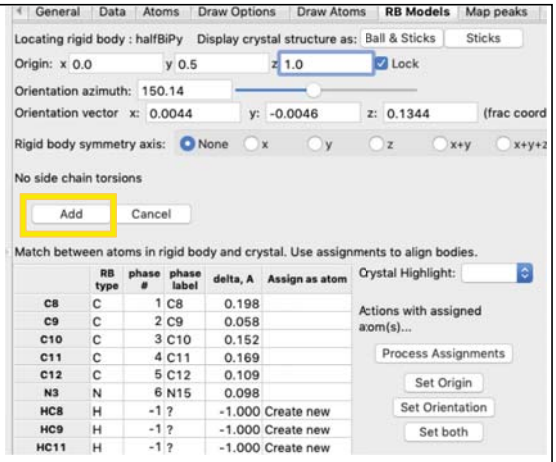
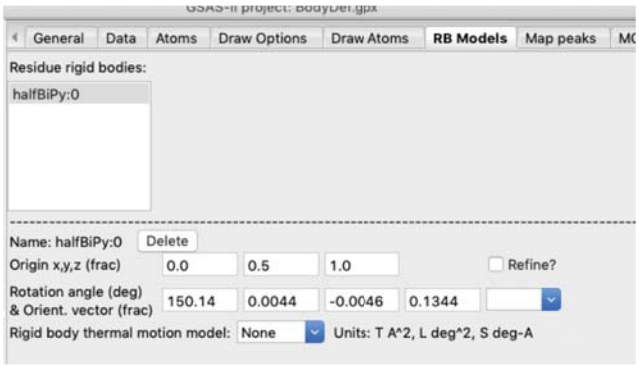
# INSERT THE BIPYRIDINE INTO THE STRUCTURE (3)

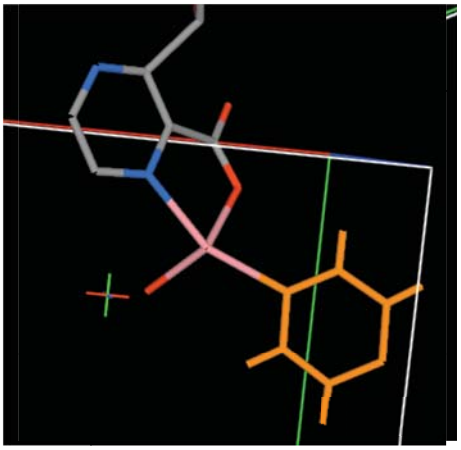
## RB has been located close to site in structure

- Adjust until all non-H atoms match within ~0.2Å
- Press “Add” to use use this origin and orientation.




The window changes to show the rigid body parameters. Rigid body bonds are shown in Orange (by default)

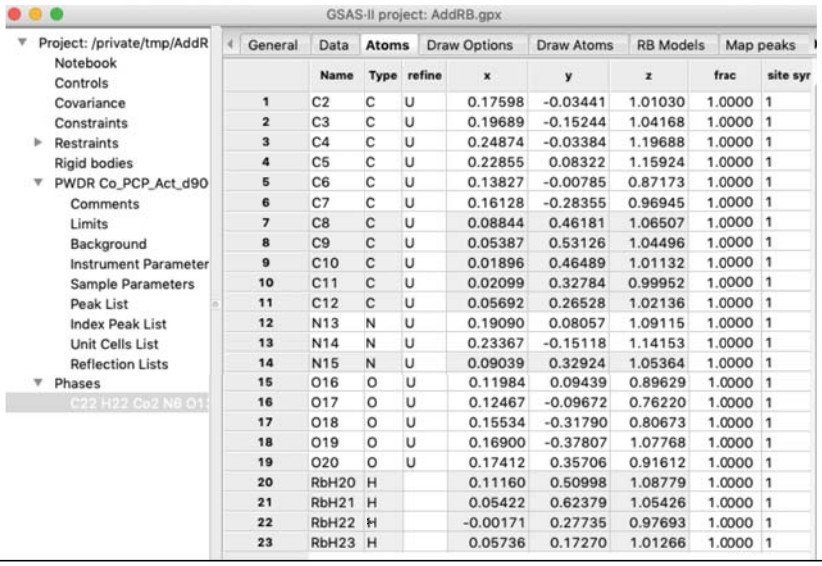


# CHANGE IN THE ATOMS TABLE

## Atoms in the rigid body are displayed in gray

- After the rigid body is added, atoms in rigid bodies are highlighted in gray in the atoms display.
  - Note that atoms added to the list when the RB was included are name “Rb…” and are placed at the end of the list.




| | Name | Type | refine | x | y | z | frac | site syr |
|---|---|---|---|---|---|---|---|---|
| 1 | C2 | C | U | 0.17598 | -0.03441 | 1.01030 | 1.0000 | 1 |
| 2 | C3 | C | U | 0.19689 | -0.15244 | 1.04168 | 1.0000 | 1 |
| 3 | C4 | C | U | 0.24874 | -0.03384 | 1.19688 | 1.0000 | 1 |
| 4 | C5 | C | U | 0.22855 | 0.08322 | 1.15924 | 1.0000 | 1 |
| 5 | C6 | C | U | 0.13827 | -0.00785 | 0.87173 | 1.0000 | 1 |
| 6 | C7 | C | U | 0.16128 | -0.28355 | 0.96945 | 1.0000 | 1 |
| 7 | C8 | C | U | 0.08844 | 0.46181 | 1.06507 | 1.0000 | 1 |
| 8 | C9 | C | U | 0.05387 | 0.53126 | 1.04496 | 1.0000 | 1 |
| 9 | C10 | C | U | 0.01896 | 0.46489 | 1.01132 | 1.0000 | 1 |
| 10 | C11 | C | U | 0.02099 | 0.32784 | 0.99952 | 1.0000 | 1 |
| 11 | C12 | C | U | 0.05692 | 0.26528 | 1.02136 | 1.0000 | 1 |
| 12 | N13 | N | U | 0.19090 | 0.08057 | 1.09115 | 1.0000 | 1 |
| 13 | N14 | N | U | 0.23367 | -0.15118 | 1.14153 | 1.0000 | 1 |
| 14 | N15 | N | U | 0.09039 | 0.32924 | 1.05364 | 1.0000 | 1 |
| 15 | O16 | O | U | 0.11984 | 0.09439 | 0.89629 | 1.0000 | 1 |
| 16 | O17 | O | U | 0.12467 | -0.09672 | 0.76220 | 1.0000 | 1 |
| 17 | O18 | O | U | 0.15534 | -0.31790 | 0.80673 | 1.0000 | 1 |
| 18 | O19 | O | U | 0.16900 | -0.37807 | 1.07768 | 1.0000 | 1 |
| 19 | O20 | O | U | 0.17412 | 0.35706 | 0.91612 | 1.0000 | 1 |
| 20 | RbH20 | H | | 0.11160 | 0.50998 | 1.08779 | 1.0000 | 1 |
| 21 | RbH21 | H | | 0.05422 | 0.62379 | 1.05426 | 1.0000 | 1 |
| 22 | RbH22 | H | | -0.00171 | 0.27735 | 0.97693 | 1.0000 | 1 |
| 23 | RbH23 | H | | 0.05736 | 0.17270 | 1.01266 | 1.0000 | 1 |

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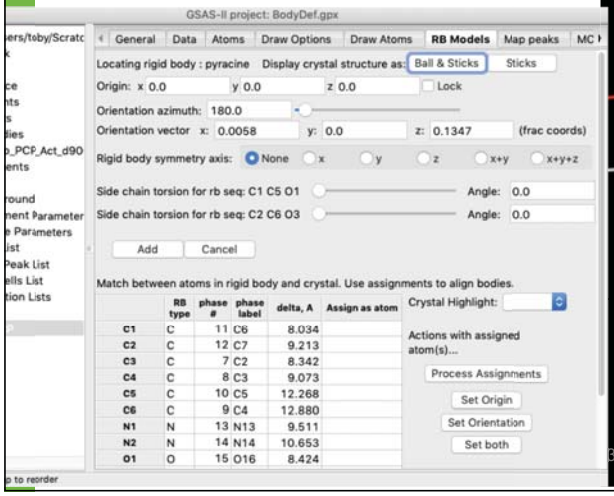
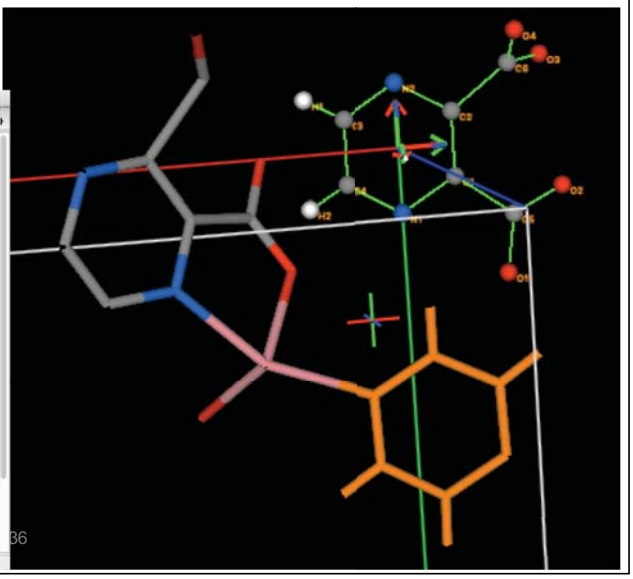
# INSERT THE PYRAZINE INTO THE STRUCTURE (1)

## Identify the body

- Go to RB Models phase tab; use “Edit Body”/“Locate and Insert Rigid Body”; select the pyrazine fragment
- Note that for this body, both the origin and orientation must be determined.




| | RB type | phase # | phase label | delta, A | Assign as atom |
|---|---|---|---|---|---|
| C1 | C | 11 | C6 | 8.034 | |
| C2 | C | 12 | C7 | 9.213 | |
| C3 | C | 7 | C2 | 8.342 | |
| C4 | C | 8 | C3 | 9.073 | |
| C5 | C | 10 | C5 | 12.268 | |
| C6 | C | 9 | C4 | 12.880 | |
| N1 | N | 13 | N13 | 9.511 | |
| N2 | N | 14 | N14 | 10.653 | |
| O1 | O | 15 | O16 | 8.424 | |



# INSERT THE PYRAZINE INTO THE STRUCTURE (2)

## Define pairs of atoms

- This time we will identify rigid atoms that should be paired with specific atoms in the structure. We will use the 1st two C and 1st two N atoms. Then press the "Set both" button for a best-fit.

Match between atoms in rigid body and crystal. Use assignments to align bodies.

| | RB type | phase # | phase label | delta, A | Assign as atom |
|---|---|---|---|---|---|
| C1 | C | 7 | C2 | 5.200 | C2 |
| C2 | C | 8 | C3 | 5.6[illegible] | C3 |
| C3 | C | 11 | C6 | 5.758 | |
| C4 | C | 12 | C7 | 7.503 | |
| C5 | C | 10 | C5 | 6.210 | |
| C6 | C | 9 | C4 | 6.763 | |
| N1 | N | 13 | N13 | 6.819 | |
| N2 | N | 14 | N14 | 7.818 | |
| O1 | O | 15 | O16 | 3.237 | |
| O2 | O | 16 | O17 | 2.835 | |
| O3 | O | 17 | O18 | 3.747 | |
| O4 | O | 18 | O19 | 3.928 | |
| H1 | H | -1 | ? | -1.000 | |
| H2 | H | -1 | ? | -1.000 | |

Crystal Highlight: C2

Actions with assigned atom(s)...

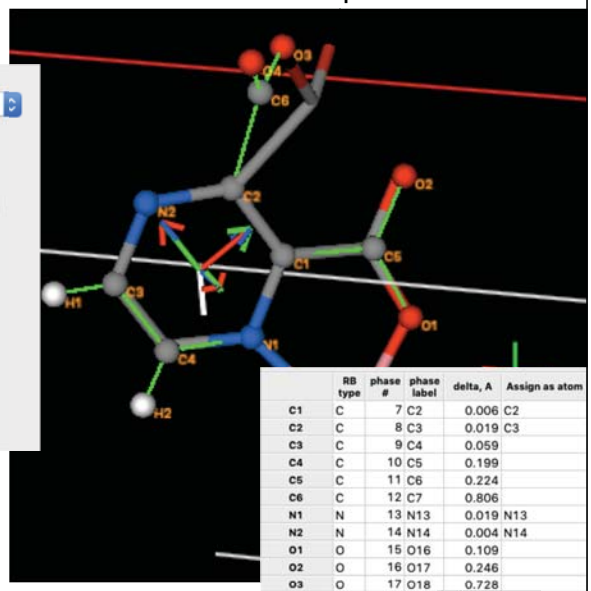
Process Assignments

Set Origin

Set Orientation

Set both

C1
C2
C3
C4
C5
C6
N13
N14
O16
O17




| | RB type | phase # | phase label | delta, A | Assign as atom |
|---|---|---|---|---|---|
| C1 | C | 7 | C2 | 0.006 | C2 |
| C2 | C | 8 | C3 | 0.019 | C3 |
| C3 | C | 9 | C4 | 0.059 | |
| C4 | C | 10 | C5 | 0.199 | |
| C5 | C | 11 | C6 | 0.224 | |
| C6 | C | 12 | C7 | 0.806 | |
| N1 | N | 13 | N13 | 0.019 | N13 |
| N2 | N | 14 | N14 | 0.004 | N14 |
| O1 | O | 15 | O16 | 0.109 | |
| O2 | O | 16 | O17 | 0.246 | |
| O3 | O | 17 | O18 | 0.728 | |
| O4 | O | 18 | O19 | 0.571 | |
| H1 | H | -1 | ? | -1.000 | Create new |
| H2 | H | -1 | ? | -1.000 | Create new |

With 4 sets of atoms paired an excellent alignment is obtained



# INSERT THE PYRAZINE INTO THE STRUCTURE (3)

## Adjust torsions

- The torsions set at 0 degrees reproduces the initial structure well, but moving the sliders shows different options.
- Press the "Add" button to insert this body.

General | Data | Atoms | Draw Options | Draw Atoms | RB Models | Map peaks | MC

Locating rigid body : pyracine  Display crystal structure as: Ball & Sticks | Sticks

Origin: x 0.21216  y -0.03513  z 1.112  Lock

Orientation azimuth: 212.46

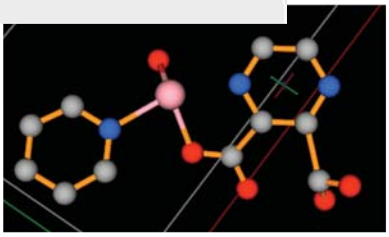
Orientation vector x: -0.0034  y: -0.0009  z: 0.1279  (frac coords)

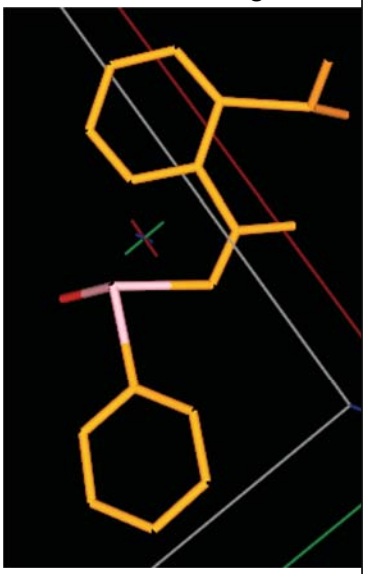
Rigid body symmetry axis: None | x | y | z | x+y | x+y+z

Side chain torsion for rb seq: C1 C5 [illegible]  Angle: 0.0

Side chain torsion for rb seq: C2 C6 [illegible]  Angle: 0.0

Add | Cancel





Bonds in rigid bodies are shown as orange lines in stick or ball-and-stick plots



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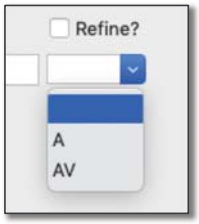
# REFINEMENT WITH RIGID BODIES

## Orientation and Origin can be refined




**Origin:** The rigid body origin can be refined or not. (In special cases it may be necessary to use a "Hold" constraint on one or two origin parameters – see next slide.)

**Orientation:** orientation is defined by a quaternion, reorganized as a unit vector and azimuthal rotation around that vector. Orientation can be refined in one of two modes: "A" or "AV".

- In "AV" mode, both the vector and azimuth are refined
- In "A" mode, only azimuthal rotation is refined. This is used when symmetry requires a particular orientation for the vector.

Example: For bipyridine, the origin cannot be refined, but for pyrazine it should be. For both, the orientation can be refined as "AV"



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# SYMMETRY SPECIAL CASES FOR RIGID BODIES

## Constraints on the Rigid Body Cartesian & Crystal origin/axes

- **Center of symmetry**: The Cartesian origin will need to be the -1 position. This always(?) will be either on an atom or at the midpoint between two atoms. Usually only one from each symmetry-related pair of atoms will be included in the body (or occupancies must be set to 0.5 due to atom duplication).
  - Crystal coordinates: The rigid body origin will be fixed as the -1 site. No constraints on orientation.
- **Mirror plane**: The normal to the mirror plane must be along a fixed Cartesian axis* and the Cartesian origin must fall in the plane. (E.g. if z is unique then the plane must be at z=0).
  - Crystal coordinates: One coordinate in the rigid body origin will need to be fixed on the mirror plane (place a hold on variable *p*::RBRP*ξ*:#:# *ξ=x, y or z*). The RB orientation vector will need to be fixed along the mirror plane normal. The RB azimuth angle can be refined.
- **Rotation axis**: The Cartesian origin must be on the axis, which will be at a midpoint between a group of atoms or on an atom. Align the axis along a fixed Cartesian axis* .
  - Crystal coordinates: coordinates for the rigid body origin will need to be constrained to stay on the axis by placing holds and/or constraints on origin parameters (*p*::RBRP*ξ*:#:# *ξ=x, y or z*) to leave one free parameter. The RB orientation vector will need to be fixed along the axis. The RB azimuth angle can be refined.

Glide planes and screw axes will require constraints similar to above only when the symmetry is internal to the molecular fragment (not common).

* Fixed Cartesian axes are x, y, z, x+y or x+y+z



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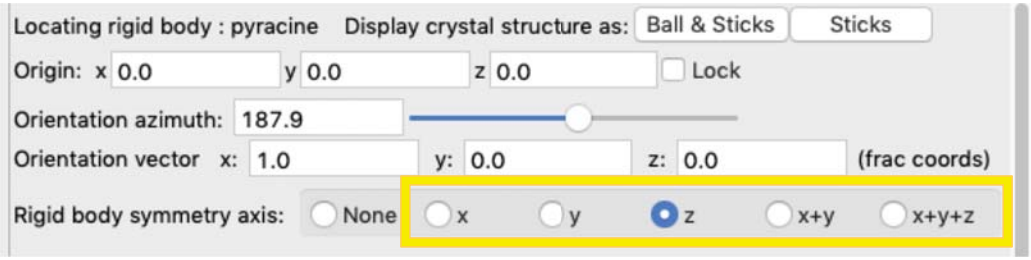
# INSERTING THE RIGID BODY: SYMMETRY SETTINGS

## For bodies on mirror planes or rotation axes

- When inserting a body with azimuthal symmetry constraints, the axis previously defined as the symmetry axis must be designated




- The orientation vector will need to be specified as well as the origin.

- The effect of rigid body angular rotation can be viewed with the azimuth slider



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# ADP FITTING FOR RIGID BODIES

## ADP = Atomic Displacement Parameters (~ thermal parameters)

Motion of rigid bodies can be described by ADPs for individual atoms or with terms that describe the possible motion associated with a rigid group of atoms. These are known as TLS terms.

- The T terms describe translational motion, which will be the same for all atoms in the group, but can differ by direction.
- The L terms describe libration, which can be thought of as frustrated rotations around the origin of the body. The further the atom is located from the body origin, the larger L will make the ADP.
- The S terms describe “screw” motion, which combines T & L motion, and is not needed if the group motion is unhindered and origin is at the center of mass.

The simplest ADP model for a rigid body is to constrain all atoms in the group to have the same Uiso value. The next most complex model is to have a single T ($T_{11}$=$T_{22}$=$T_{33}$) & single L term ($L_{11}$=$L_{22}$=$L_{33}$). I sometimes use a few T & L terms, but never more than that (with powder data).



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# OTHER RIGID BODY TRICKS

- It can be useful to combine restraints with rigid body constraints. For the example structure, restraints can be placed on the Co-O and Co-N bond distances, which places further restrictions to prevent the refinement from overfitting.

- Rigid Body torsions will not move H atoms as riders. If H atoms are needed, use Edit Atoms/"on selected atoms…"/"Calc H atoms" to generate H atoms on riders.

- On occasion I have needed to have two rigid bodies that have a fixed connection with each other, but still have degrees of freedom. To do that in GSAS/EXPGUI, I define the bodies so that they share an origin at the point which joins them. I then constrain the origin of the two groups to refine together. This is probably not needed in GSAS-II, since both groups of atoms can be placed in a single body with a torsion between them.



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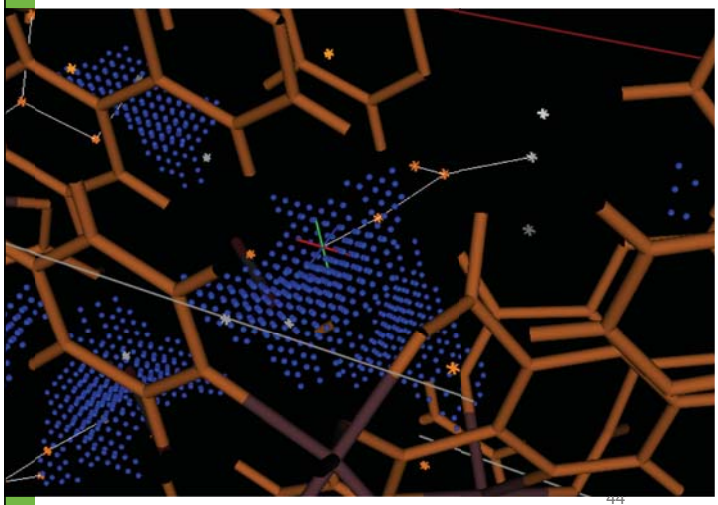
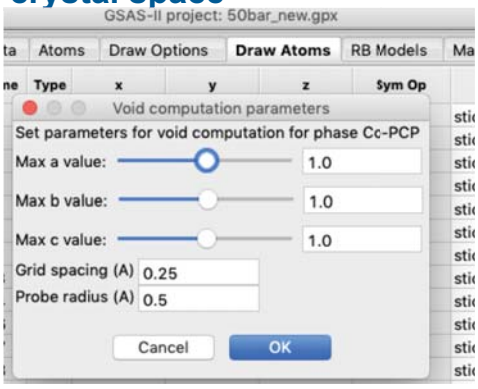
# OTHER NICE TOOLS FOR GUEST/SOLVENT MOLECULE STRUCTURES

## Understanding the spatial environment in crystal space

Void space visualizer: "Edit Figure"/"Create Void Map" (in Draw Atoms)

- Resulting map shows regions of space without atoms





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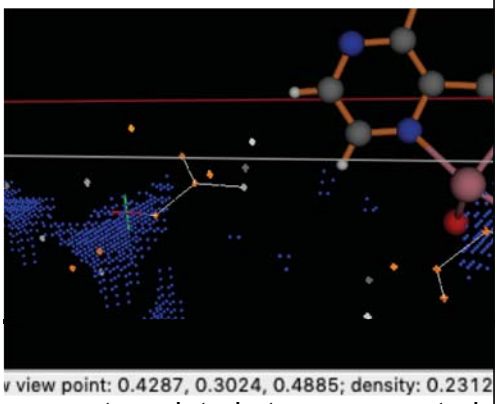
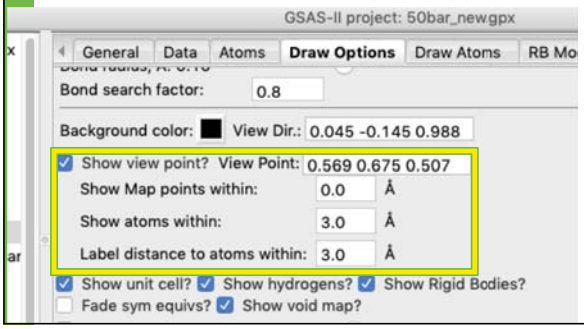
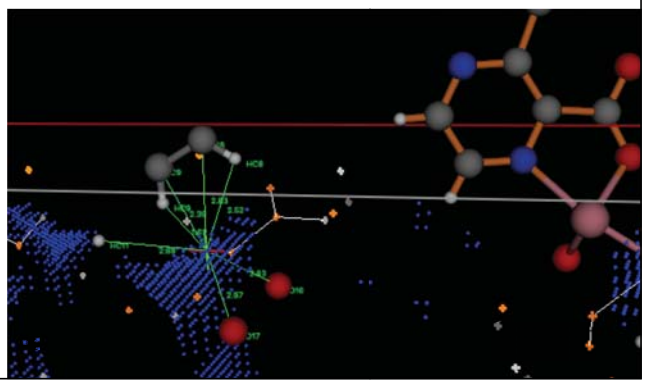
# OTHER NICE TOOLS FOR GUEST/SOLVENT MOLECULE STRUCTURES

## Using the View Point




- By default, the view point is set to (½,½,½)
- Move view point using right mouse button
  - Movement in in screen x-y
  - Rotate drawing (left mouse) for 3rd dimension
  - Position is shown in bottom frame
  - Reset to (½,½,½) by pressing “c” key
  - Type in coordinates on Draw Options
- Optionally, highlight distances around view point; symmetry-related atoms generated

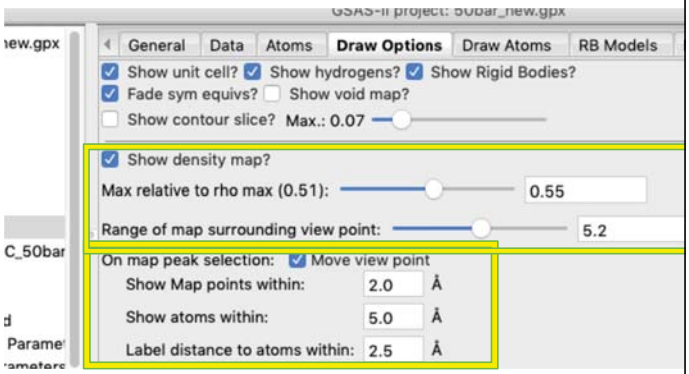


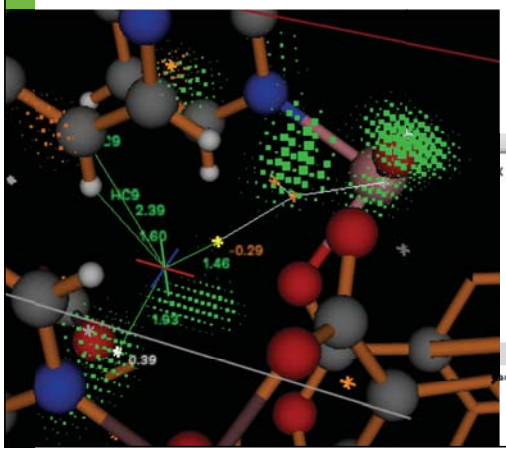



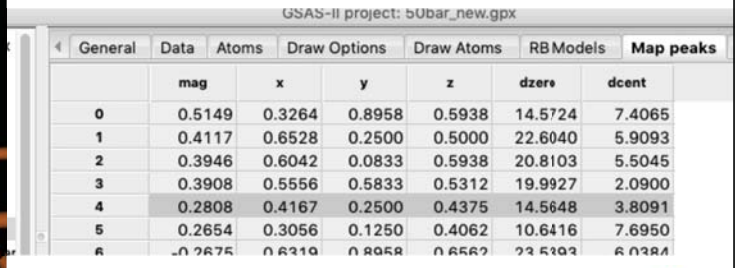
# OTHER NICE TOOLS FOR GUEST/SOLVENT MOLECULE STRUCTURES

## New feature: understand Fourier map peaks

- Highlight distances around a selected Fourier map peak
- Note distances are labeled as set in Draw Options
- Also, optionally show map



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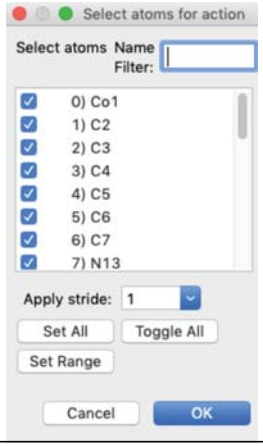
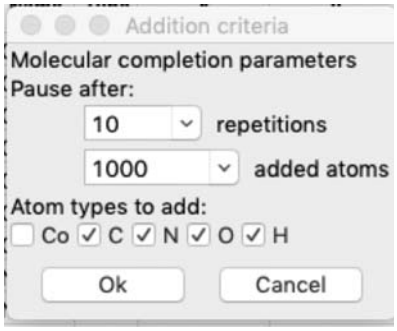
# A FEW OTHER NEW VISUALIZATION/MAP FEATURES

- Map peaks (Map peaks menu)
  - Equivalent peaks: finds peaks related by symmetry to a selected peak
  - Unique Peaks: brings one symmetry-unique peak to top of list

- Draw Atoms (Edit Figure menu)
  - Complete Molecule: Adds atoms bonded to selected atoms already in draw list



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## CONCLUSIONS

Rigid bodies are fun, perhaps not easy, but very useful

GSAS-II has two very powerful rigid body implementations

New GSAS-II tools make them much easier to create and use



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