

A GUIDE TO MAKING ANIMATED REACTIONS

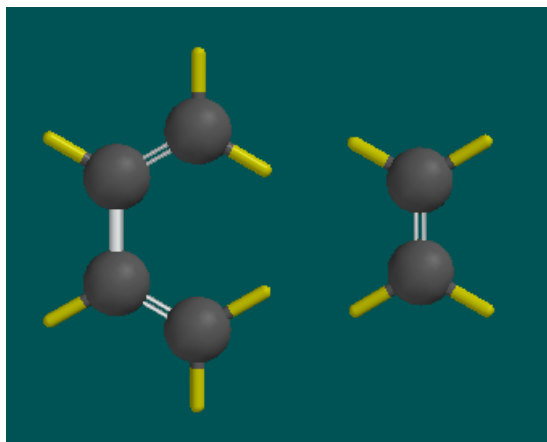
Contained within these pages is a simple guide on how to make your own interactive reactions. There are several techniques that can be used to construct these animations; it all really depends on the molecules involved in the chosen reaction.

The steps involved in producing these animations will be explained using a simple diels-alder reaction as an example, that of ethylene and 1,3-butadiene.

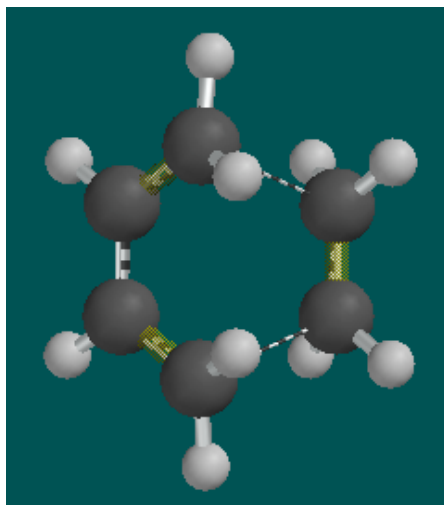
NOTE: This guide is specific for a Mac computer and some of the options may vary from that of a PC.

- **Finding the transition state:**

Open up 'SPARTAN' and on a blank page construct the two molecules relatively close together as shown below: (*Make sure you are comfortable with the use of Spartan*)



From here select the '*transition state*' arrow option and move the relative electrons into the positions that you require. Once this is done press the R⇒P button to give something similar to below:



Under the *setup* menu select *calculations*. Tick the *frequencies* option, and if any of the molecules possess a charge, adjust that setting as required. Select the *transition-state geometry* option and the level of calculation you wish to perform. A good starting block is always the *Hartree-Fock, 3-21G* option. However, if this produces undesirable results, a higher level of calculation may work better, but takes much longer. *Semi-Empirical* methods are also good for some examples, either *AM1* or *PM3*. To increase the number of steps to perform, type *OPTCYCLES=X* into the options box. (*X indicates the number of iterations*). Submit the calculation.

Calculations

Calculate:
Transition State Geometry at: Ground state IRC
with: Hartree-Fock 3-21G Pseudopotential

Start from:
Initial geometry.

Subject to:
 Constraints Frozen Atoms Symmetry
Total Charge: Neutral
Multiplicity: Singlet

Compute:
 UV/vis IR NMR

Print:
 Orbitals & Energies Thermodynamics Vibrational Modes Atomic Charges

Options:
OPTCYCLES=5000 Converge

Apply Globally

Once the calculation is complete, click on *spectra* from under the *display* menu. Check that there is only one imaginary frequency and select it. (*The imaginary frequency is at the top of the list indicated with an (i), and for this example should be about 818.85*). If the vibration resembles that which you would expect for the reaction then proceed as described below, if not, a different level of calculation is required, try *Hartree-Fock, 6-31G**.

Finding the transition state geometry is performed in this way for all examples.

- **Producing the IRC: (Intrinsic reaction coordinate)**

For very simply molecules it is possible to find the IRC using Spartan directly. To do this simply tick the *IRC* box on the *calculations* screen, and perform the calculation again. That said, for most examples this just produces static models, making its use very limited.

A much more successful way to produce an IRC involves using ‘**GAMESS**’ and ‘**MacMolPlt**’. Through Spartan, export the transition state geometry structure as a .xyz file. From here, open up the .xyz file in MacMolPlt and under *edit* select *copy coordinates*.

Now using a text program, such as Text Wrangler, open up a new page and copy the contents of the table below onto the page:

```
$CONTRL SCFTYP=RHF RUNTYP=hessian COORD=UNIQUE
MAXIT=200 ICHARG=0 MULT=1 exetyp=run $END
$STATPT OPTTOL=1.0E-5 purify=.t. hssend=.t. $END
$BASIS GBASIS=N21 NGAUSS=3 NDFUNC=1 $END
$FORCE purify=.t. $END
$irc saddle=.t. npoint=50 FORWRD=.f. $end
$GUESS GUESS=HUCKEL $END
$SYSTEM MWORDS=2 $END
$DATA
C1
$END
```

Be sure to copy this exactly, including all the spaces that are present. If the reaction has a charged component, be sure to change the ‘**ICHARG=0**’ command accordingly, and for larger molecules, alter the number in the

'**\$\$SYSTEM MWORDS=2**' command to about 5, which should be adequate for most examples.

Now insert the coordinates of the transition state in between the **C1** and **\$END** command, which will give the following:

```
$CONTRL SCFTYP=RHF RUNTYP=hessian COORD=UNIQUE
MAXIT=200 ICHARG=0 MULT=1 exetyp=run $END
$STATPT OPTTOL=1.0E-5 purify=.t. hssend=.t. $END
$BASIS GBASIS=N21 NGAUSS=3 NDFUNC=1 $END
$FORCE purify=.t. $END
$irc saddle=.t. npoint=50 FORWRD=.f. $end
$GUESS GUESS=HUCKEL $END
$$SYSTEM MWORDS=2 $END
$DATA

C1
C 6.0 1.41299999 -0.30739999 0.69730002
C 6.0 1.41299999 -0.30739999 -0.69730002
C 6.0 0.54759997 0.47770000 -1.41240001
H 1.0 1.94729996 -1.08889997 -1.20560002
H 1.0 0.24380000 1.43620002 -1.04340005
H 1.0 0.47790000 0.36370000 -2.47860003
C 6.0 0.54759997 0.47770000 1.41240001
H 1.0 1.94729996 -1.08889997 1.20560002
H 1.0 0.47790000 0.36370000 2.47860003
H 1.0 0.24380000 1.43620002 1.04340005
H 1.0 -1.30309999 -1.16890001 1.22259998
C 6.0 -1.40890002 -0.24710000 0.68790001
C 6.0 -1.40890002 -0.24710000 -0.68790001
H 1.0 -1.91760004 0.53460002 1.22060001
H 1.0 -1.30309999 -1.16890001 -1.22259998
H 1.0 -1.91760004 0.53460002 -1.22060001
$END
```

Save this text file with .inp at the end.

Now from the terminal open up the gamess directory and run gamess for the file that has just been saved. (*The command is ./gms followed by the file name*). Once this has completed there should now be three files, the original .inp file, along with a new .log and .dat file. (**NOTE:** *If there is a problem with the process and gamess fails to give the required results, the problem is usually mentioned in the .log file*). From the .dat file locate the portion of the text which starts **\$HESS**. Below this there should be a long list of numbers eventually ending with **\$END**. Highlight and copy all the text between these two points, including the \$HESS and \$END commands.

From here open up a new text page and copy the contents of the box below onto the page. Insert the correct transition state geometry coordinates and the \$HESS to \$END data where appropriate: *(Remember to adjust the 'ICHARG=0' and '\$SYSTEM MWORDS=2' commands if necessary)*

```

$CONTRL SCFTYP=RHF RUNTYP=irc COORD=UNIQUE
MAXIT=200 ICHARG=0 MULT=1 exetyp=run $END
$STATPT OPTTOL=1.0E-5 purify=.t. hssend=.t. $END
$BASIS GBASIS=N21 NGAUSS=3 NDFUNC=1 $END
$FORCE purify=.t. $END
$irc saddle=.t. npoint=50 FORWRD=.f. $end
$GUESS GUESS=HUCKEL $END
$SYSTEM MWORDS=2 $END
$DATA

C1
C 6.0 1.41299999 -0.30739999 0.69730002
C 6.0 1.41299999 -0.30739999 -0.69730002
C 6.0 0.54759997 0.47770000 -1.41240001
H 1.0 1.94729996 -1.08889997 -1.20560002
H 1.0 0.24380000 1.43620002 -1.04340005
H 1.0 0.47790000 0.36370000 -2.47860003
C 6.0 0.54759997 0.47770000 1.41240001
H 1.0 1.94729996 -1.08889997 1.20560002
H 1.0 0.47790000 0.36370000 2.47860003
H 1.0 0.24380000 1.43620002 1.04340005
H 1.0 -1.30309999 -1.16890001 1.22259998
C 6.0 -1.40890002 -0.24710000 0.68790001
C 6.0 -1.40890002 -0.24710000 -0.68790001
H 1.0 -1.91760004 0.53460002 1.22060001
H 1.0 -1.30309999 -1.16890001 -1.22259998
H 1.0 -1.91760004 0.53460002 -1.22060001
$END

$HESS
...
...
...
...
$END

```

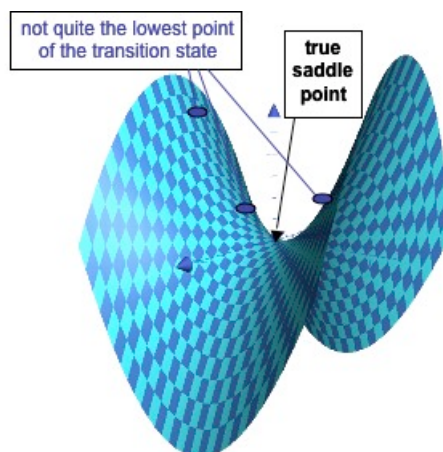
Again save this text as a .inp file and run it as shown previously. This first calculation will produce the first half of the IRC. Once the calculation has run, open up the .irc file in MacMolPlt to check that what has been produced is reasonable. If the IRC is as expected, the above text file needs to only be slightly altered to find the second half of the IRC. All that need to be changed is the '**FORWRD=.f.**' command, replacing the **f** with a **t**. Run this

file through gamess and check that this is also as expected. If it is, the two files can be manipulated together to give the overall IRC for the reaction.

Saddle point calculations:

For a lot of examples the correct IRC cannot always be found straight off. This is usually because the coordinates of the transition state are incorrect or they are not quite accurate enough.

Consider the diagram below. If you treat the overall reaction as a mountain pass, where at one side we have the reactants and the other the products, you would ideally want to find the lowest route over. However, Spartan does not always find the lowest route, and when this happens, additional calculations need to be run to find the 'true' saddle point (i.e. the lowest energy path to the products).



If after running an IRC calculation you find that it has failed, running a '*sadpoint*' calculation can often help to find the true saddle point. Start by returning to the *.inp* file that you used to run the IRC calculation. This should include both the original transition state coordinates and the hessian data. Simply change the '**RUNTYPE**' of this file from '*irc*' to '*sadpoint*' (as shown below), and save this as a new input file. Run the new file through gamess and once it has finished a new set of files will have been created. To find the new transition state coordinates simply open the new *.log* file in MacMolPlt, and copy the coordinates of the final frame into a new gamess file. Repeat the process as described earlier to find the hessian data, and ultimately, run another IRC calculation with the new coordinates.

```

$CONTRL SCFTYP=RHF RUNTYP=sadpoint COORD=UNIQUE
MAXIT=200 ICHARG=0 MULT=1 exetyp=run $END
$STATPT OPTTOL=1.0E-5 purify=.t. hssend=.t. $END
$BASIS GBASIS=N21 NGAUSS=3 NDFUNC=1 $END
$FORCE purify=.t. $END
$irc saddle=.t. npoint=50 FORWRD=.f. $end
$GUESS GUESS=HUCKEL $END
$SYSTEM MWORDS=2 $END
$DATA

```

```

C1
C 6.0 1.41299999 -0.30739999 0.69730002
C 6.0 1.41299999 -0.30739999 -0.69730002
C 6.0 0.54759997 0.47770000 -1.41240001
H 1.0 1.94729996 -1.08889997 -1.20560002
H 1.0 0.24380000 1.43620002 -1.04340005
H 1.0 0.47790000 0.36370000 -2.47860003
C 6.0 0.54759997 0.47770000 1.41240001
H 1.0 1.94729996 -1.08889997 1.20560002
H 1.0 0.47790000 0.36370000 2.47860003
H 1.0 0.24380000 1.43620002 1.04340005
H 1.0 -1.30309999 -1.16890001 1.22259998
C 6.0 -1.40890002 -0.24710000 0.68790001
C 6.0 -1.40890002 -0.24710000 -0.68790001
H 1.0 -1.91760004 0.53460002 1.22060001
H 1.0 -1.30309999 -1.16890001 -1.22259998
H 1.0 -1.91760004 0.53460002 -1.22060001
$END

```

```

$HESS
...
...
...
...
$END

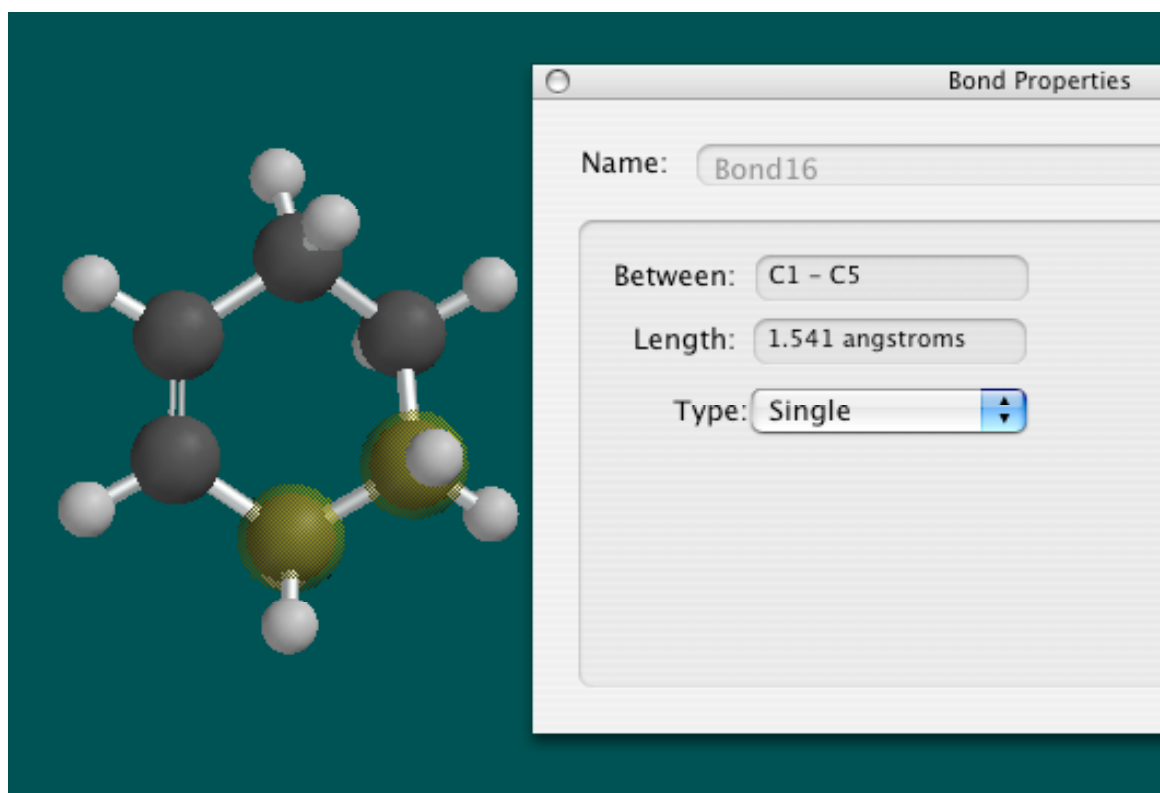
```

Occasionally the true saddle point may still not have been found, in this case, repeat the process again to see if this makes a difference, or if not, consider reviewing the original model of the transition state, and perhaps adjust the orientation.

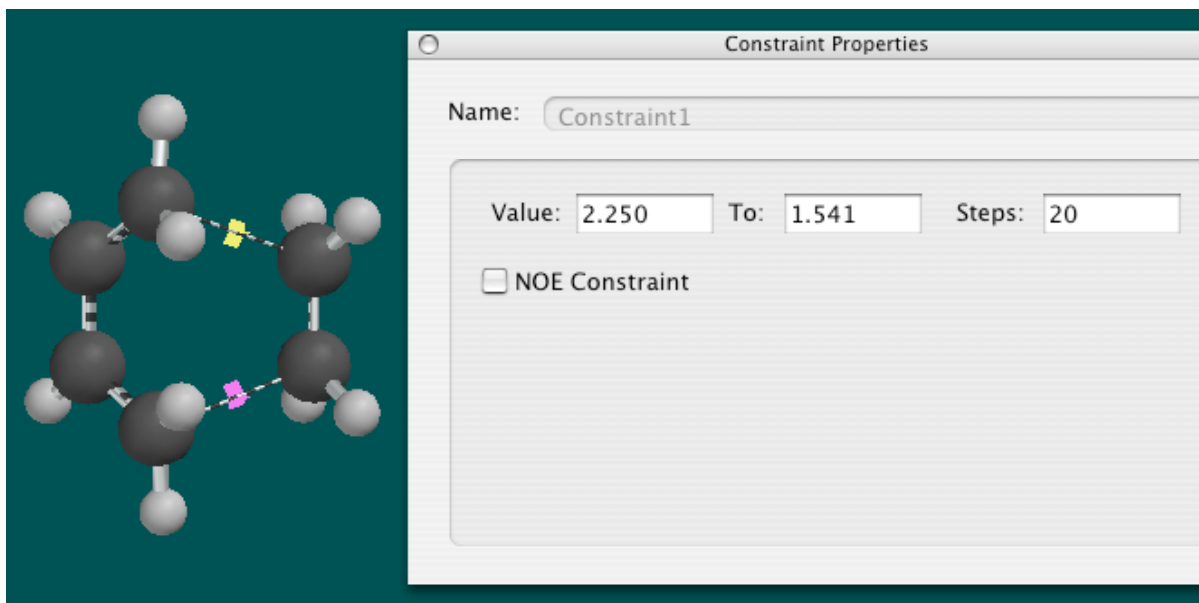
- **Coordinate driven approach:**

For some examples it may be simpler to take a coordinate driven approach, producing an energy profile.

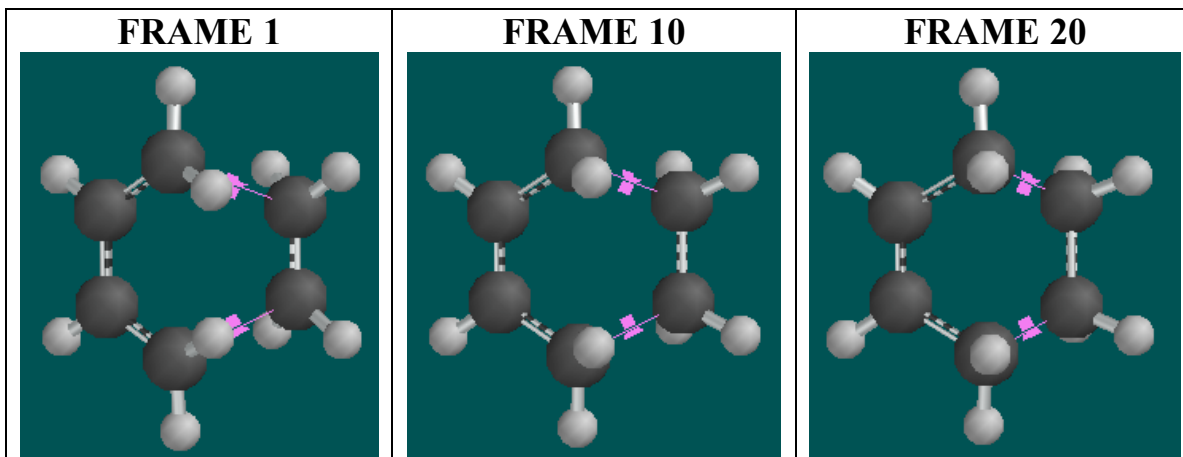
Once the transition state geometry has been found for the reaction, various different constraints can be set to the different bonds. The most accurate and convenient way to find out what the constraints should be is to run an ***equilibrium geometry*** calculation for the products and reactants. This will allow you to see what the bond lengths should be for all of the different components. Construct the molecules and then from the ***setup*** menu select ***calculations***. For most examples it is adequate to run a ***Hartree-Fock, 3-21G*** calculation, and once this has completed the bond lengths, angles, etc, can be measured.



As you can see the bond length for the newly formed bond in our example is 1.541. So setting a bond constraint on the two newly forming bonds of the ***transition state geometry*** model, between a value greater than 1.541 to indicate the reactant phase, (*In this case about 2.25*) and a value of 1.541 as the product, should produce a very accurate energy profile. (*Select the number of step you require, usually about 20 is enough*).



Once the two constraints have been set, from the *setup* menu select *calculations* and run the *energy profile* option, using the same level of calculation as you did for the transition state geometry calculation. Once the calculation has run, a new file is saved and opens automatically on the screen, this is the energy profile, and it can then be exported as a .xyz file.



- **Useful commands to manipulate the animations in jmol:**

To set the type of bond that you want to appear between atoms at different lengths, use the command:

connect A B (atomno=X) (atomno=Y) TYPE;

A and B are the distances between the atoms you want this to have an effect at; X and Y are the numbers of the atoms in question; TYPE indicates which type of bond, PARTIAL, SINGLE, DOUBLE, AROMATIC or TRIPLE.

To select specific bond characteristics, i.e. a particular bond width, use the following command:

select atomno=X or atomno=Y or atomno=Z;FEATURE;

X, Y and Z are the atom numbers; FEATURE includes things such as *'wireframe 0.1'* and *'spacefill 15%'*.

To draw a curly arrow, type into the console of jmol:

draw arrow1 arrow {1 1 1} {2 2 2} (atomno=3)

To manipulate the arrow type:

set picking draw

Hold the 'alt' key to move the arrow where desired, and find the details of the arrow by typing

show draw

in the console.

A recent feature to the *chemtube3d* web site is the inclusion of charge and lone pair labels throughout the animations. The following instructions must be included at the beginning of any command (*just after the load file command*) in order for the labels to behave correctly:

select all;set labelOffset 0 0;font label 18 serif bold;color label orange;set fontScaling TRUE;

These instructions basically allow the labels to appear in the centre of the molecule with the required font and at an appropriate size. It also allows the labels to stay relative when the molecule is zoomed in and out. The following command allows for individual molecules in particular frames to be labeled:

select atomno=X and model=1.Y;label Z;

Where X is the atom number, Y is the frame number, and Z is the required label.

This command allows you to characterize a bond between two particular atoms (e.g. Its color or width), but not however the atoms themselves:

select atomno=X or atomno=Y;set bondmode AND;color bonds COLOUR;wireframe Z;

- **Script commands:**

It has been found that in certain browsers, if the commands within the image maps are too long, then they won't load correctly or at all. In these cases it is best to relocate the command to an independent file, which the image map can then be linked to. The easiest way to do this is to create a 'script' folder within the website folder which the larger commands can be saved in. An example of how the command should be written is shown below:

```
load model/fragmentation/stereochemistry/sub_cyclohexane/cis/1.xyz;wireframe 0.1;spacefill 20%;moveto 0.0 52 105 993 163.51;select all;set labelOffset 0 0;font label 18 serif bold;color label orange;set fontScaling TRUE;connect (atomno=21) (atomno=26) DOUBLE;connect (atomno=21) (atomno=27) DOUBLE;connect 1.385 1.445 (atomno=2) (atomno=3) AROMATIC;connect 1 1.384 (atomno=2) (atomno=3) DOUBLE;connect 1.76 2.31 (atomno=2) (atomno=4) PARTIAL;connect 1.435 1.5 (atomno=4) (atomno=7) AROMATIC;connect 1 1.434 (atomno=4) (atomno=7) DOUBLE;connect 1.72 1.88 (atomno=7) (atomno=18) PARTIAL;wireframe 0.1;select atomno=3 and model=1.1;label ;;select atomno=3 and model=1.2;label ;;select atomno=3 and model=1.3;label ;;select atomno=3 and model=1.4;label ;;select atomno=3 and model=1.5;label ;;select atomno=3 and model=1.6;label ;;select atomno=3 and model=1.25;label +;select atomno=3 and model=1.26;label +;select atomno=3 and model=1.27;label +;select atomno=3 and model=1.28;label +;select atomno=3 and model=1.29;label +;select atomno=3 and model=1.30;label +;select atomno=3 and model=1.31;label +;select atomno=3 and model=1.32;label +;select atomno=3 and model=1.33;label +;select atomno=3 and model=1.34;label +;select atomno=3 and model=1.35;label +;select atomno=3 and model=1.36;label +;select atomno=3 and model=1.37;label +;select atomno=3 and model=1.38;label +;select atomno=3 and model=1.39;label +;select atomno=3 and model=1.40;label +;select atomno=3 and model=1.41;label +;select atomno=3 and model=1.42;label +;select atomno=18 and model=1.25;label -;select atomno=18 and model=1.26;label -;select atomno=18 and model=1.27;label -;select atomno=18 and model=1.28;label -;select atomno=18 and model=1.29;label -;select atomno=18 and model=1.30;label -;select atomno=18 and model=1.31;label -;select atomno=18 and model=1.32;label -;select atomno=18 and model=1.33;label -;select atomno=18 and model=1.34;label -;select atomno=18 and model=1.35;label -;select atomno=18 and model=1.36;label -;select atomno=18 and model=1.37;label -;select atomno=18 and model=1.38;label -;select atomno=18 and model=1.39;label -;select atomno=18 and model=1.40;label -;select atomno=18 and model=1.41;label -;select atomno=18 and model=1.42;label -;select atomno=2 or atomno=4;set bondmode AND;color bonds green;wireframe 0.14;draw arrow1 ARROW {2.5258636 2.2316608 -0.005033493} {1.8705454 2.3119926 0.20354843} {1.6806698 1.960289 0.10418701} {2.174943 1.5223303 -0.21914673};draw arrow2 ARROW {1.2922058 0.87216187 -0.14969254} {1.2107038 0.36396027 0.2987442} {0.77132034 0.03902626 0.35229874} {0.17572784 0.24547005 -0.07335663};draw arrow3 ARROW {-0.906559 -0.38713646 0.02225113} {-0.60072136 -0.7089081 0.5097141} {-0.77900505 -0.8256035 0.8187847} {-1.4413223 -0.5691376 0.71840286};draw fill noMesh noDots notFrontOnly fullylit;color draw opaque [xffa500];
```

The file should be saved as a *.txt* file. When the command is written directly on the image map, the command is placed after the *href="* " " command. However, this needs to be changed accordingly when the command is placed in a script folder. An example of one such script command is shown below, where the link would be changed according to where the file is located:

```
<area shape="rect" coords="1,2,174,55" href="javascript:jmolScript('script  
script/fragmentation/stereochemistry/sub_cyclohexane/cis/1.txt')" />
```

Script linking is extremely useful for commands with a considerable number of labels, or one that has a larger number of arrows or additional drawings.



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