## 9.3: Computational Instructions

The goal of this computational exercise is to compute the C-H BDE values of each unique type of C-H bond in norbornane and use this information to shed insight on the "unexpected" selectivity of shown in its radical chlorination. To compute these BDE values, we will need the enthalpies of the parent norbornane, the norbornyl radicals produced in hydrogen atom abstraction, and the hydrogen radical (H·). With this information, we can compute the BDE values for each unique type of hydrogen atom on norbornane. You will be provided with the enthalpy values for the parent norbornane and the hydrogen atom (H). You will need to calculate the enthalpy values associated with radicals formed by the abstraction of each unique type of hydrogen on norbornane. As shown in Figure 8, there are 4 unique types of hydrogen on norborane and the removal of any one of these hydrogens will produce a unique radical. The radicals are numbered so that they represent the chlorinated product they would make with a "rad" subscript. For example, $\mathbf{3_{rad}}$ is the radical that would make product **3**.

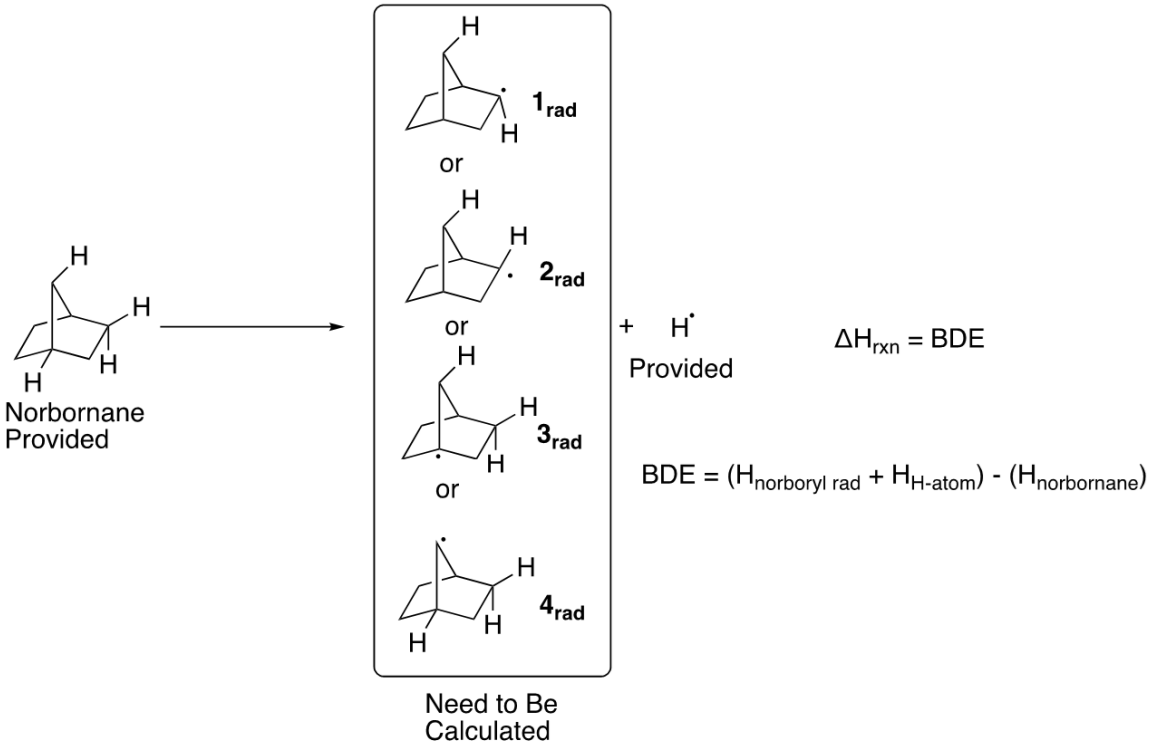


Figure 8. Species whose enthalpy values are provided and those that need to be calculated.

The process for calculating the enthalpy for the radical species is identical for each calculation. To illustrate this process, we will walk through the calculation of the enthalpy for $\mathbf{1_{rad}}$ as shown in Figure 8. The three other calculations can then be performed using the same process.

Start by creating a folder on your desktop and naming it BDE exercise. Within this folder create 4 subfolders named *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]*. Next you should download generic.inp and norbornane.xyz, which are the supporting files for this exercise. Save a copy of the generic input file within each of the subfolders that you have created. You can save the norbornane.xyz within the BDE exercise folder. The file structure described is illustrated in Figure 9.

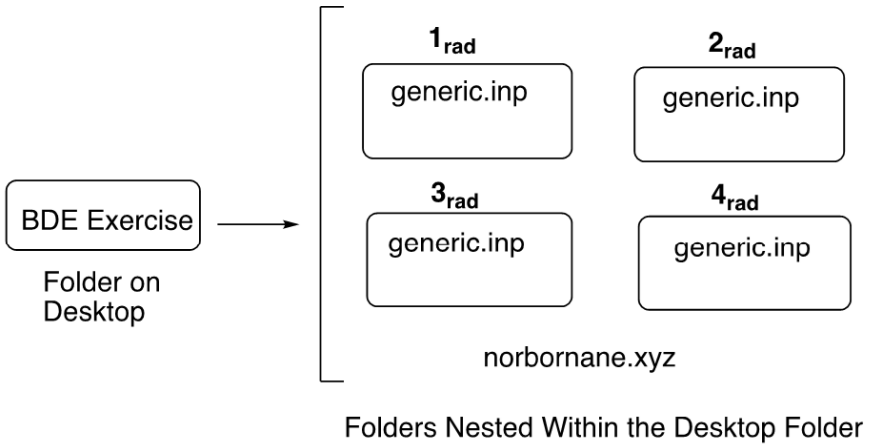


Figure 9. Representation of the file structure used in this exercise.

Next, you should open norbornane.xyz in Avogadro. Click on the selection button (looks like an arrow) and select the exo hydrogen on carbon 2, as shown in Figure 10. The hydrogen will turn blue. Delete this atom by pressing backspace to create the coordinates for *[Math Processing Error]*. Save the new structure as 1rad_coord.xyz within the 1rad subfolder.

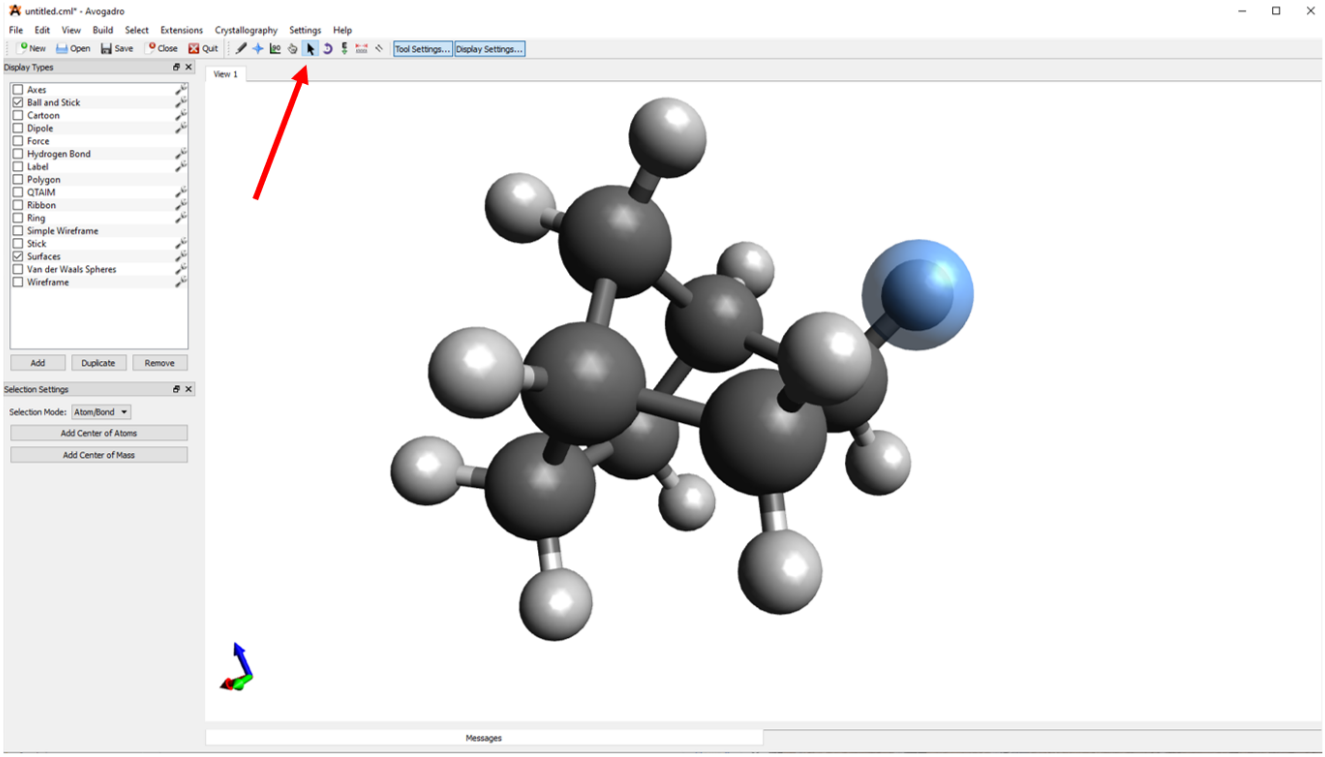

Figure 10. Norbornane shown in Avogadro with the 2-exo hydrogen selected. The selection button is indicated by a red arrow.

Next, you should open the generic input file within **1rad** folder. As shown in Figure 11, the text of the file is very similar to energy calculations that we have done in previous exercises. Briefly, the first line of the input file begun with a # is a comment where you can indicate the type of calculation being performed. The second line that starts with an ! symbol indicates the functional (B3LYP) and basis set (DEF2-SVP) for the calculation. Moreover, it tells the computer we want to perform a geometry optimization (OPT) and a frequency calculation (FREQ). The final line of text tells the computer that we want to use a .xyz file for coordinates and that the compound has a charge of 0 with a spin multiplicity of 2. The spin multiplicity of the system, *[Math Processing Error]*, is equal to the sum of the absolute value of spin quantum numbers, *[Math Processing Error]* (remember that each unpaired spin has a value of ½) times 2 plus 1. For example, a molecule without any unpaired spin would have an *[Math Processing Error]* (singlet) because the sum of the spin quantum numbers (+1/2 and -1/2) is zero. An organic radical (7 electrons, which results in one unpaired

electron or net ½ spin) would have an *[Math Processing Error]* (doublet), and a diradical such as dioxygen would have an *[Math Processing Error]* (triplet).

*[Math Processing Error]*

Finally, the generic script has the name of the .xyz coordinates file upon which the computer will run the calculation. To allow our calculation to run successfully you need to change generic_coord.xyz to the name of the coordinates file of the species you are investigating. In this case you should change generic_coord.xyz to 1rad_coord.xyz.

```
# comment (what we are trying to calculate)
!B3LYP def2-SVP FREQ OPT

* xyzfile 0 2 generic_coord.xyz
```

Figure 11. Generic input script for the calculation of the energy of a norbornyl radical. You should change generic_coord.xyz to the name of the coordinates file you are looking to use. In the case we are working on together it should be 1rad_coord.xyz.

We can now run our calculation using Orca via the command line. Briefly, open the command prompt to your PC by right clicking on the start button and searching for command prompt. First, we need to tell the computer to look on the C drive and we do this by typing C: and hitting enter. Next, we need to tell the computer where the input script and the coordinates file are to run the calculation. We do this by typing cd (space) and pasting the file path. When you hit enter the computer will paste a new line indicating that the current directory has changed, as shown in Figure 12A. To find the file path of your input script, right click on the input script (1rad.inp) and select properties. The file path will appear under location, and you can highlight and copy this file path (Figure 12B).

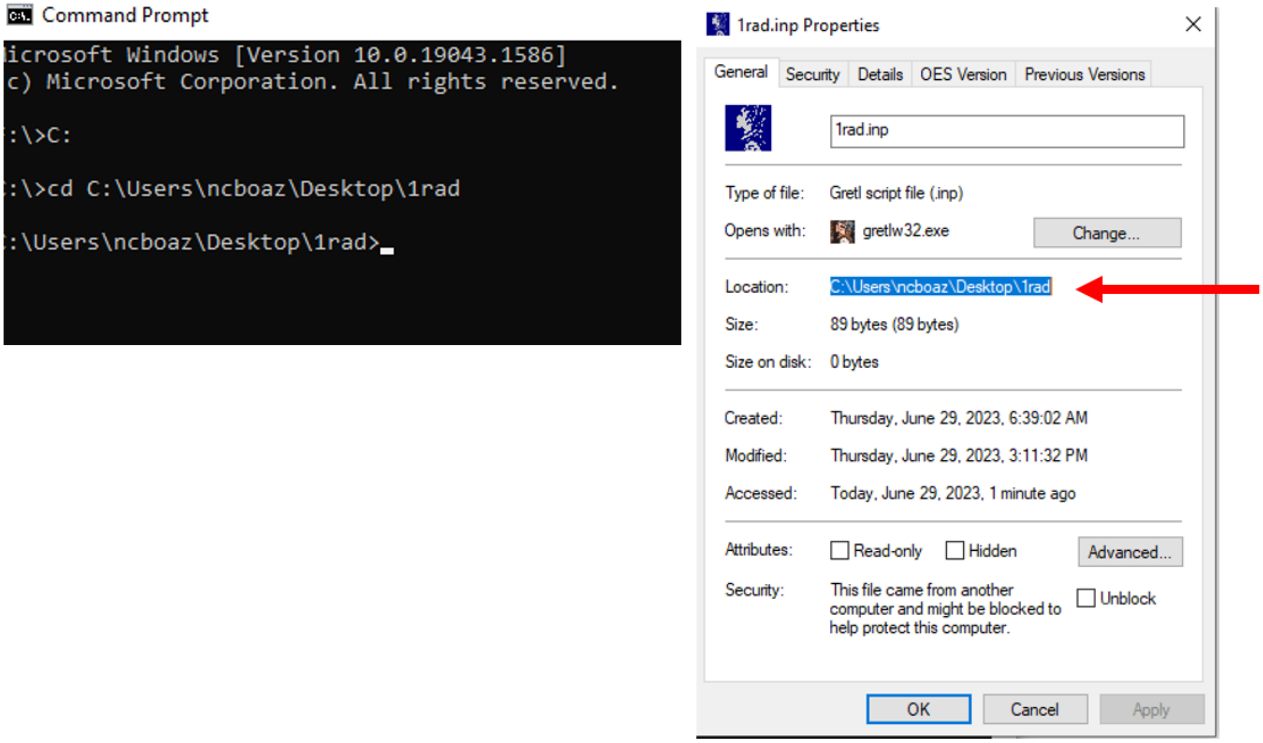


Figure 12. (Left) Changing of the file path in the command prompt to match the location of our input script. 12B. (Right) Locating the file path on the properties window of the input script (Red Arrow).

Next, we will run the calculation by typing orca 1rad.inp > 1rad.out and pressing enter. After pressing enter it may not appear that much is happing, but your computer is working on the calculation and the folder 1rad will quickly become populated with the output of your calculation. Depending upon the speed of your computer, the calculation will take about 30-45 minutes, and upon completion the command prompt will print another line indicating that it is ready for the next command (Figure 13). Given the time it takes to complete this calculation it is a good idea to run more than one calculation at the same time by opening a new command

prompt window. Alternatively, if you are working in a group, assign different computations to different group members and compare your results at the end.

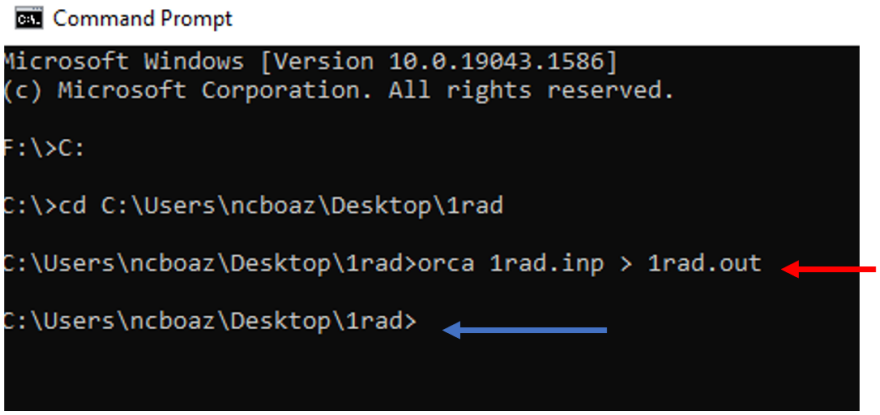


Figure 13. Running the calculation using the command line. The line indicated by the red arrow shows the computer that we want to use Orca to calculate the commands in 1rad.inp and that the results of this calculation should be placed in the output file 1rad.out. The line indicated by the blue arrow is the computer indicating that the calculation is complete, and the command prompt is ready for the next command.

You can now find the enthalpy value for the norbornyl radical **1rad** by opening 1rad.out in notepad. Scroll to the end to find the Thermochemistry section of the results and under the ENTHALPY header you can find the enthalpy value of **1rad** in Hartree, as shown in Figure 14.

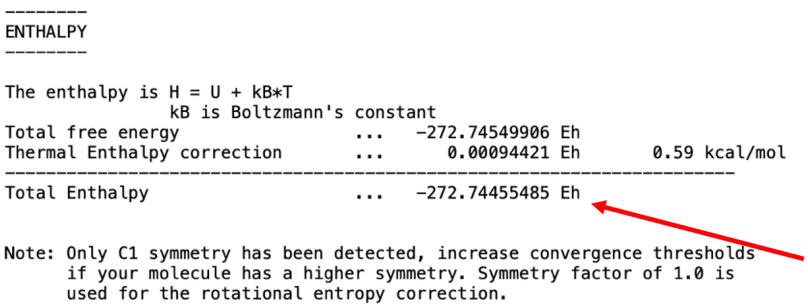


Figure *[Math Processing Error]*: Copy and Paste Caption here. (Copyright; author via source)

Finally, you can view the optimized geometry of your calculated radical species by opening the output file (.out file extension) with Avogadro as shown in Figure 15. Note the geometry on the carbon containing the radical.

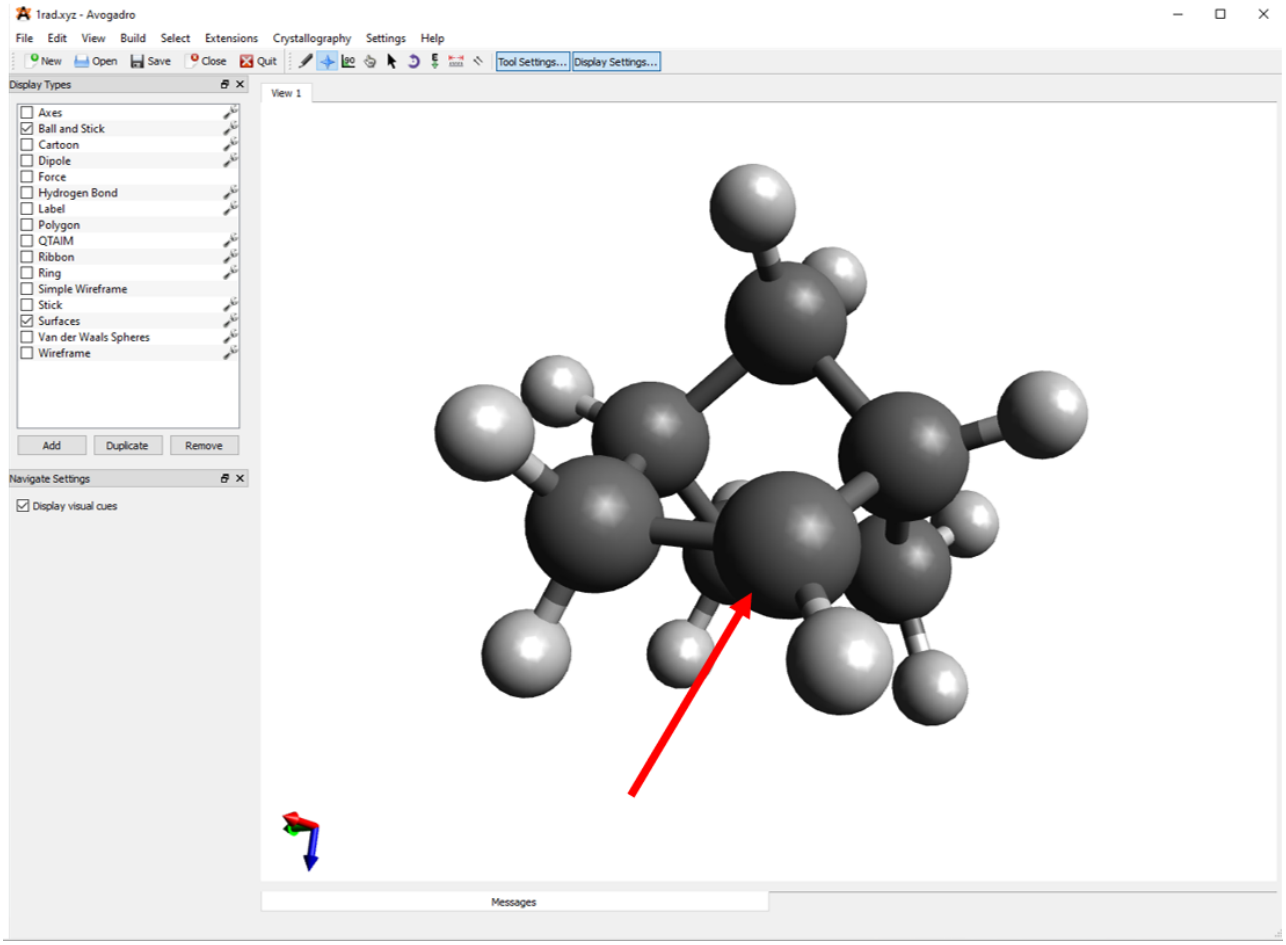


Figure 15. Output structure of the norbornyl radical with the unpaired electron centered on carbon 2. The radical is centered on the carbon indicated by a red arrow.

## References


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