

## Ab Initio Quantum Chemical Computation II: cis-trans Isomerization Barrier for N,N-dimethylacetamide

### Purpose:

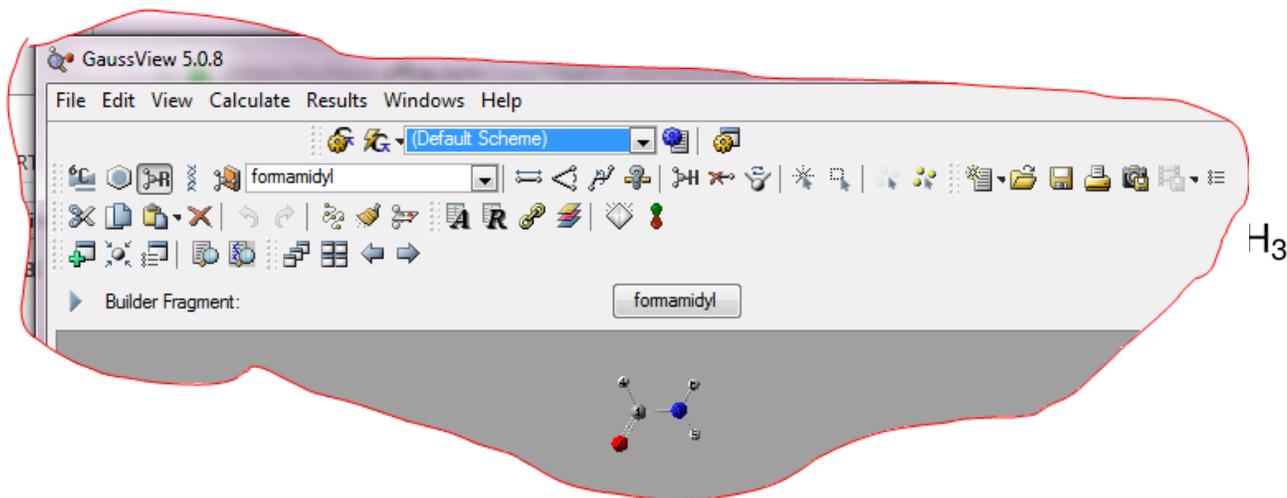
Using Gaussian09, compute the activation energy for the cis-trans isomerization of N,N-dimethylacetamide (NNDMA), which was determined from NMR line widths vs. temperature last week.

### Background:

Refer to the handout 374Computation18.pdf from March 7, 2018, as needed.

1. Using GaussView, create NNDMA as follows:

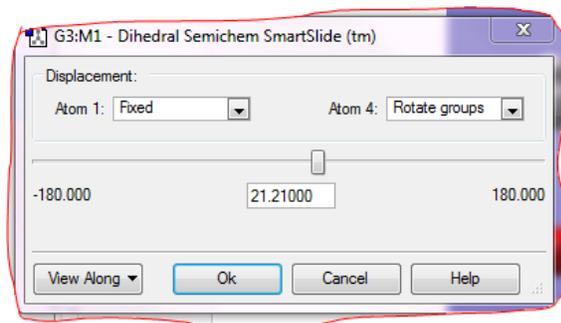
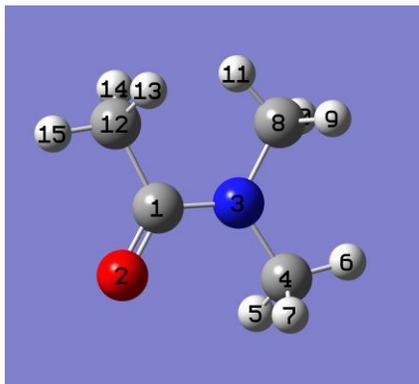
a. control-N gives a new window



b. click on **R-group Fragment Icon**, (see above) and select **formamidyl**. Then click on the blank window.

c. To add the methyls, click on **Element Fragment** (upper left hand icon) twice, select C and choose the **tetrahedral** form. Click on each of the H atoms to add the methyls in the **order: N cis to O, N trans to O and C. (If you use a different order, you will be SORRY!) A different order will cause many of the instruction below to be wrong.** [It is not necessary, but you could use the **Modify bond** to make partial double bonds for the C-O and C-N bonds. This in no way affects the calculation, but in GaussView, if you now click the **“Clean”** icon (a whisk broom, ha-ha), the structure will be altered to a planar form, to reflect the pi electron resonance.]

The structure should now look like the image on the left below.



d. We want to start in a non-planar geometry by changing what is called a “*dihedral angle*” involving atoms 4 3 1 2 = 20 (or -20) degrees, just to see if the lowest energy will be planar as expected. We choose to do this with GaussView graphically, for the experience. (It could be done as, you will see, by modifying the .gjf file with any text editor.)

e. We want to rotate about the 3-1 bond by 20 degrees. Rotation about bonds is usually quantified by a *dihedral angle*, usually defined by a sequence of atoms in which the middle 2 atoms define the bond about which rotation happens. To do this, **click on the dihedral icon** , and then click on atoms 4 3 1 2 (or, equivalently 2 1 3 4). Choose to keep the first atom clicked to be “**Fixed**” and the 4<sup>th</sup> atom clicked to “**Rotate groups**” as seen in the image on the right above. Slide the bar to see what happens and leave it at a value of 20-25 degrees.

**IMPORTANT:** You can eyeball the angle pretty closely: *The angle itself is the clockwise rotation of either the 1<sup>st</sup> or 4<sup>th</sup> atom, whichever is more distant as you look down the line formed by the 2<sup>nd</sup> and 3<sup>rd</sup> atoms.*

f. Save the file as NNDMA20, in **Z-matrix form**. (*Cartesian coordinate box is not checked*)

**2.** Optimize the geometry starting slightly non-planar. (If you were to start planar, nothing will happen even if planar was the maximum energy)

Open and edit the NNDMA20.gjf file in **wordpad** so the top 4 lines look like what is below. The lines below the 0 1 (charge and multiplicity) is the “**Z-matrix**”.

```
# opt hf/3-21g pop=reg nosym
```

```
twisted 20 degrees
```

```
0 1
```

```
C
```

```
O
```

N	1	B1					
C	3	B3	1	A2	2	D1	0
H	4	B4	3	A3	1	D2	0
H	4	B5	3	A4	1	D3	0
H	4	B6	3	A5	1	D4	0

C	3	B7	1	A6	2	D5	0
H	8	B8	3	A7	1	D6	0
H	8	B9	3	A8	1	D7	0
H	8	B10	3	A9	1	D8	0
C	1	B11	2	A10	3	D9	0
H	12	B12	1	A11	2	D10	0
H	12	B13	1	A12	2	D11	0
H	12	B14	1	A13	2	D12	0

B1	1.24307702
B2	1.36696598
B3	1.47000000
B4	1.07000000
B5	1.07000000
B6	1.07000000
B7	1.47000000
B8	1.07000000
B9	1.07000000
B10	1.07000000
B11	1.54000000
B12	1.07000000
B13	1.07000000
B14	1.07000000
A1	121.94678701
A2	120.61576986
A3	109.47120255
A4	109.47120255
A5	109.47123134
A6	121.17018857
A7	109.47120255
A8	109.47120255
A9	109.47123134
A10	123.09373276
A11	109.47120255
A12	109.47120255
A13	109.47123134
<b>D1</b>	<b>20.00000000</b>
D2	59.98943140
D3	179.98944620
D4	-60.01056120
<b>D5</b>	<b>-160.00855560</b>
D6	120.09840828
D7	-119.90157692
D8	0.09841568
D9	-179.99883400
D10	119.99109248
D11	-120.00889273
D12	-0.00890012

**The Z-matrix** requires some introduction:

**a.** There is no format requirement for the Z-matrix except for the following rules.

--no blank line after charge and multiplicity  
--must be a blank line between the first (symbolic) and second (numeric) sections  
-- the numbers in the second section (Bond lengths, bond Angles, and Dihedral angles MUST have decimal point.  
--there MUST be a blank line following the numbers section.  
--no blank lines anywhere else for this calculation.

**b.** In the first section, the atom symbol order also denotes the atom number (could be atomic numbers instead of symbols.) atom 1 is chosen somewhat arbitrarily and is always placed at the origin. Here we pick the carbonyl C as atom 1 because the Fragment came already numbered that way. It is possible to renumber if you wanted to.

atom 2 is the O and B1 connects atom 1 and 2

atom 3 is N and B2 connects atom 3 to atom 1; the angle A1 is defined by atoms 3-1-2

atom 4 is C connected to atom 3 by B3, angle is A2 = 1-3-4 and dihedral D1= 2-1-3-4

The others follow the pattern of atom 4.

**c.** Check that D1 = the angle you made to be ~ 20 deg.  
and that the line involving atom 8 has D5= D1 – 180. , i.e., about -160.

**3.** Run G09W using this file. That may take about a minute.  
Examine the NNDMA20.out file. You should see that it ended up planar.

**4.** Now twist the dihedral to 90 degrees to approximate the transition state (top of the barrier to cis-trans isomerization. Create a new file starting with a copy of the file that you just ran, but with the D1 dihedral frozen and the route card should say **popt** (for partial optimization) **instead of opt**. We freeze D1 at 90.0 degrees by modifying the Z-matrix so that the last few lines look like:

```
....  
A11      109.47120255  
A12      109.47120255  
A13      109.47123134  
D1        20.00000000  
D2        59.98943140  
D3       179.98944620  
D4        -60.01056120  
D5       -160.00855560  
D6       120.09840828  
D7       -119.90157692  
D8         0.09841568  
D9       -179.99883400  
D10      119.99109248  
D11      -120.00889273  
D12       -0.00890012
```

```
constants
D1          90.0
```

**5.** Leave a blank line after the last line. This freezes the twist angle at 90 but allows all the other bond lengths and angles to seek minimum energy, because the pi bonding is destroyed by the twist and the amino group may no longer be expected to be planar. Save this file as NNDMA-90, and run G09W to get the energy.

The energy difference from the two calculations will yield a rough approximation to the activation energy for the cis-trans isomerization. It will not be a very good approximation because the hf/3-21g method/basis set is too simple, but the job will run quickly.

**6.** From the .out file, find the optimized energy in atomic units (hartrees) for the planar and twisted forms. These will be the number following the first **SCF Done: E(RHF) =** several lines above the line stating **“Stationary point found”**. Look up the conversion between hartrees and kJ/mol using Wikipedia, or other source.

**7.** Rerun the last two calculations with a better method and basis set, to get a better prediction of the activation energy. Change each file only by changing **hf/3-21g to b3lyp/6-31(d)**

**8.** Compare the predicted activation energy values in kJ/mole that you obtained with the two computational methods.

**9.** Compare these computed activation energies with what you deduced from our kinetics experiment for the cis-trans isomerization done last week.

**10.** With GaussView, examine the structures from the b3lyp/6-31g(d) NNDMA calculations, and note particularly whether the heavy atoms lie in a plane or not in the lowest energy state, whether the amino is planar or pyramidal in the twisted geometry, and whether the C=O and C-N bond lengths change as one might expect if these bonds change from partial single-double bonds to pure double and single in the twisted geometry.