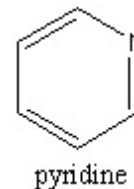


### 3 Choice of Theoretical Method

#### Exercise 1 Determine the Proton Affinity for Pyridine using PM3.

Open GaussView.

Construct pyridine by double clicking the Ring Fragment icon (1<sup>st</sup> row, 2<sup>nd</sup> across), clicking the pyridine fragment (2<sup>nd</sup> row, 2<sup>nd</sup> across) and clicking in the View workspace. C<sub>5</sub>H<sub>5</sub>N appears.



Click Calculate / Gaussian and choose Job: Opt+Freq and defaults; Method: Semiempirical, PM3, and defaults, Title: pyridine PM3; Link 0: PYRIDINEPM3.chk and defaults; defaults for other tabs.

Click Submit. Save as PYRIDINEPM3.gjf. Click OK.

After the job is completed, click Yes twice and open PYRIDINEPM3.chk. Click Results / Summary to see the summary of the calculations.

Close everything but the main Control Panel.

Open the PYRIDINEPM3.log file using a text editor such as WordPad and scroll to the bottom. Scroll up about 300 lines (~10 clicks on the scroll bar) and locate the line “Sum of electronic and thermal Enthalpies”. Record this value  $H(\text{C}_5\text{H}_5\text{N}) =$  \_\_\_\_\_ Eh.

Close the log file.

Click File / New / Create MolGroup.

Click the Ring Fragment icon and choose benzene (1<sup>st</sup> row, 1<sup>st</sup> across) and click in the View workspace. C<sub>6</sub>H<sub>6</sub> appears.

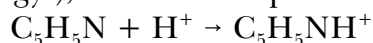
Click the Element Fragment icon twice and choose N. Click N atom (1<sup>st</sup> across) and click one of the C atoms in the benzene. C<sub>5</sub>H<sub>5</sub>NH<sup>+</sup> appears.

Optimize at the PM3 level as above. Save as HPYRIDINEPM3.chk and HPYRIDINEPM3.gjf. Be sure that the charge is 1 in the Method window.

Close everything but the main Control Panel.

Open the HPYRIDINEPM3.log file and record the value of “Sum of electronic and thermal Enthalpies”  $H(\text{C}_5\text{H}_5\text{NH}^+) =$  \_\_\_\_\_ Eh.

Given the “Sum of electronic and thermal Enthalpies” of H<sup>+</sup> is  $H(\text{H}^+) = 0.002368$  Eh (note: no electronic energy!), calculate the proton affinity  $\Delta_r H = \text{PA}$  for



using  $\text{PA} = \{H(\text{C}_5\text{H}_5\text{NH}^+) - [H(\text{C}_5\text{H}_5\text{N}) + H(\text{H}^+)]\}(625.5095) =$  \_\_\_\_\_ kcal mol<sup>-1</sup>.

The literature value is  $-219.2 \pm 1.7$  kcal mol<sup>-1</sup>. Calculate the percent difference = \_\_\_\_\_.

#### Exercise 2 Determine the Proton Affinity for Pyridine using Hartree-Fock.

Click File / Recent Files / PYRIDINEPM3.chk.

Click Calculate / Gaussian and choose Opt+Freq for the Job; Hartree-Fock and 6-31G(d) for the method and basis set; and give the calculation an appropriate title.

Submit and save the files as PYRIDINEHF.gjf and PYRIDINEHF.chk.

The calculations will require a few minutes to complete.

Close everything but the main Control Panel.

Record the value  $H(C_5H_5N) = \underline{\hspace{2cm}}$  Eh from the .log file.

Likewise, open HPYRIDINEPM3.chk and submit the job as HPYRIDINEHF.gjf and HPYRIDINEHF.chk.

Close everything but the main Control Panel.

Record the value of  $H(C_5H_5NH^+) = \underline{\hspace{2cm}}$  Eh.

Calculate the proton affinity PA  $\underline{\hspace{2cm}}$  kcal mol<sup>-1</sup> and the percent difference =  $\underline{\hspace{2cm}}$ .

### **Exercise 3 Determine the Proton Affinity for Pyridine using B3LYP/6-31G(d).**

Click File / Recent Files / PYRIDINEHF.chk.

Click Calculate / Gaussian and choose Opt+Freq for the Job; DFT, B3LYP and 6-31G(d) for the method and basis set; and give the calculation an appropriate title.

Submit and save the files as PYRIDINEDFT.gjf and PYRIDINEDFT.chk.

The calculations will require a few minutes to complete.

Close everything but the main Control Panel.

Record the value  $H(C_5H_5N) = \underline{\hspace{2cm}}$  Eh from the .log file.

Likewise, open HPYRIDINEHF.chk and submit the job as HPYRIDINEDFT.gjf and HPYRIDINEDFT.chk.

Close everything but the main Control Panel.

Record the value of  $H(C_5H_5NH^+) = \underline{\hspace{2cm}}$  Eh.

Calculate the proton affinity PA  $\underline{\hspace{2cm}}$  kcal mol<sup>-1</sup> and the percent difference =  $\underline{\hspace{2cm}}$ .

Close everything but the main Control Panel.