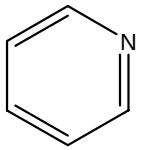
3 Choice of Theoretical Method

Exercise 1 Determine the Proton Affinity for Pyridine using AM1.



pyridine

Using the "ball and cylinder" view, build a molecule of C_5H_5N using sp^2 C and N atoms. Clean up the structure by selecting Beautify / comprehensive.

Save as pyram1.csf. Calculate $\Delta_f H$ by selecting Experiment / New and selecting chemical sample optimized geometry using AM1 geometry. Record the value _____ kcal mol^{-1} and save the structure.

Build the $C_5H_5NH^+$ structure by adding a H atom to the N atom and placing a +1 charge on the N atom. Clean up the structure by selecting Beautify / Comprehensive.

Save as hpyram1.csf. Calculate $\Delta_f H$ by selecting Experiment / New and selecting chemical sample optimized geometry using AM1 geometry. Record the value _____ kcal mol^{-1} and save the structure.

Given $\Delta_f H$ = 367.161 kcal mol^{-1} for H^+, calculate the $\Delta_r H$ = PA for

$$C_5H_5N + H^+ \rightarrow C_5H_5NH^+$$

using $\Delta_r H = \Delta_f H(C_5H_5NH^+) - [\Delta_f H(C_5H_5N) + \Delta_f H(H^+)]$ = _____ kcal mol^{-1}.

The literature value is -219.2±1.7 kcal mol^{-1}. Calculate the percent difference = _____.

Exercise 2 Determine the Proton Affinity for Pyridine using PM3.

Using the "ball and cylinder" view, build a molecule of C_5H_5N using sp^2 C and N atoms. Clean up the structure by selecting Beautify / Comprehensive.

Save as pyrpm3.csf. Calculate $\Delta_f H$ by selecting Experiment / New and selecting chemical sample optimized geometry using PM3 geometry. Record the value _____ kcal mol^{-1} and save the structure.

Build the $C_5H_5NH^+$ structure by adding a H atom to the N atom and placing a +1 charge on the N atom. Clean up the structure by selecting Beautify / Comprehensive.

Save as hpyrpm3.csf. Calculate $\Delta_f H$ by selecting Experiment / New and selecting chemical sample optimized geometry using PM3 geometry. Record the value _____ kcal mol^{-1} and save the structure.

Given $\Delta_f H$ = 367.161 kcal mol^{-1} for H^+, calculate the $\Delta_r H$ = PA for

$$C_5H_5N + H^+ \rightarrow C_5H_5NH^+$$

using $\Delta_r H = \Delta_f H(C_5H_5NH^+) - [\Delta_f H(C_5H_5N) + \Delta_f H(H^+)]$ = _____ kcal mol^{-1}.

Calculate the percent difference = _____.

Exercise 3 Determine the Proton Affinity for Pyridine using B88LYP/DZVP.

Using the "ball and cylinder" view, build a molecule of C_5H_5N using sp^2 C and N atoms. Clean up the structure by selecting Beautify / Comprehensive.

Save as pyrdft.csf. Optimize the structure by selecting Experiment / New and selecting chemical sample optimized geometry using B88-LYP DFT geometry. (This calculation may take several minutes.)

Calculate the thermodynamic properties of the molecule by selecting Experiment / New and selecting chemical sample IR transitions using B88-LYP DFT IR spectra. (This calculation may take several minutes.)

Navigate to the pyrdft.io folder and open Dgauss Log using Word Pad. Record the enthalpy at 298 K and save the structure. H = _____ h.

Build the $C_5H_5NH^+$ structure by adding a H atom to the N atom and placing a +1 charge on the N atom. Clean up the structure by selecting Beautify / Comprehensive.

Save as hpyrdft.csf. Optimize the structure by selecting Experiment / New and selecting chemical sample optimized geometry using B88-LYP DFT geometry. (This calculation may take several minutes.)

Calculate the thermodynamic properties of the molecule by selecting Experiment / New and selecting chemical sample IR transitions using B88-LYP DFT IR spectra. (This calculation may take several minutes.)

Navigate to the hpyrdft.io folder and open Dgauss Log using Word Pad. Record the enthalpy at 298 K and save the structure. H = _____ h.

Given $H(H^+)$ = 1.481 kcal mol^{-1}, calculate the $\Delta_r H$ for

$$C_5H_5N + H^+ \rightarrow C_5H_5NH^+$$

using $\Delta_r H = [H(C_5H_5NH^+) - H(C_5H_5N)](627.51 \text{ kcal mol}^{-1}/\text{h}) + H(H^+)$ = _____ kcal mol^{-1}.

Calculate the percent difference = _____.