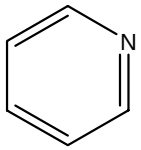
3 Choice of Theoretical Method

Exercise 1 Determine the Proton Affinity for Pyridine using AM1.



pyridine

Open / HyperChem.

Build a molecule of C_5H_5N. Double click the Draw Tool and choose C. Draw a hexagon of C atoms connected by single bonds. Double click one of the bonds to make the ring aromatic (a circle inside the hexagon will appear). Choose N and click on one of the C atoms to change it to the N atom.

Double click the Select Tool.

Save as pyram1.HIN.

Minimize using AM1 by clicking Setup / Semiempirical and click AM1. Choose Compute / Geometry Optimization and click OK. Be sure that the Status Line indicates CONV=YES.

Click Compute / Properties / Total Energy: Details and record the value of $\Delta_f H$ = _____ kcal mol^{-1}.

Save the structure.

Build the $C_5H_5NH^+$ structure by selecting the N atom and placing a +1 charge on it. Click the N atom and click Build / Set Formal Charge / +1.

Double click the Select Tool.

Save as hpyram1.HIN.

Minimize using AM1 geometry. Record the value of $\Delta_f H$ = _____ 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 = _____.

Close the workspace.

Exercise 2 Determine the Proton Affinity for Pyridine using PM3.

Open pyram1.HIN and save as pyrpm3.HIN.

Calculate $\Delta_f H$ using PM3 geometry. Record the value of $\Delta_f H$ = _____ kcal mol^{-1} and save the structure.

Close the workspace.

Open hpyram1.HIN and save as hpyrpm3.HIN.

Calculate $\Delta_f H$ using PM3 geometry. Record the value of $\Delta_f H$ = _____ 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 = _____.

Close the workspace.

Exercise 3 Determine the Proton Affinity for Pyridine using *ab initio* Methods.

Open pyrpm3.HIN and save as pyrdft.HIN.

Click Setup / Density Functional. Choose 6-31* for the Orbital Basis Set. Click Exchange Correlations / B3-LYP and click OK. Click OK.

Click Compute / Geometry Optimization.

Click Run. (This calculation may take several hours.) Record the value of E = _____ kcal mol^{-1} shown in the Status Line.

Save the structure.

Open hpyrpm3.HIN and save as hpyrdft.HIN.

Calculate the minimum energy as above. Record the value of E = _____ kcal mol^{-1}.

Save the structure.

Calculate the $\Delta_r H$ for

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

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

Calculate the percent difference = _____.