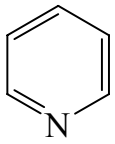
3 Choice of a Theoretical Model (Spartan)

Exercise 1 Determine the Proton Affinity of Pyridine using AM1



Using the "Entry" level, build pyridine using appropriate hybridizations for C and N.
To close the ring, go to Build / Make Bond and click on the empty valences on C and N.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical AM1, Print Orbitals and Energies.
Click Submit. Save as pyram1.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Click Display / Output and scroll down to find the Heat of Formation value. Record this value in the space labeled **(1)** below.
Save and Close the file.
Click on New File.
Using the "Expert" level, build $C_5H_5NH^+$ using appropriate hybridizations.
Click on Display / Properties and set the Total Charge to Cation.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3, Print Orbitals and Energies.
Click Submit. Save as hpyram1.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Click Display / Output and scroll down to find the Heat of Formation value. Record this value in the space labeled **(2)** below.
Given $\Delta_fH = 367.161$ kcal mol^{-1} for H^+, calculate the Δ_rH = PA for: $C_5H_5N + H^+ \rightarrow C_5H_5NH^+$
using $\Delta_rH = \Delta_fH\{C_5H_5NH^+\} - [\Delta_fH\{C_5H_5N\} + \Delta_fH\{H^+\}]$ = _____ kcal mol^{-1}.

Δ_rH = **(2)**_____ - [**(1)** _____ + (367.161 kcal mol^{-1}] = _____kcal mol^{-1}.
Using the literature value of -219.2 ±1.7 kcal mol^{-1}, calculate the % difference. _____

Exercise 2 Determine the Proton Affinity of Pyridine using PM3
Repeat the above process, but replace "AM1" with "PM3" in the calculations window.
$\Delta_rH = \Delta_fH\{C_5H_5NH^+\} - [\Delta_fH\{C_5H_5N\} + \Delta_fH\{H^+\}]$ = _____ kcal mol^{-1}.

Δ_rH = **(4)**_____ - [**(3)** _____ + (367.161 kcal mol^{-1})] = _____kcal mol^{-1}.
Using the literature value of -219.2 ±1.7 kcal mol^{-1}, calculate the % difference. _____

Exercise 3 Determine the Proton Affinity of Pyridine using DFT B3LYP 6-31G*
Repeat the above process, but replace 'Semi-Empirical" with "Density Functional" and "AM1" with "B3LYP 6-31G*. In this case, the energy you need will be found by choosing Display / Properties. Use the following formula to calculate Δ_rH for the protonation reaction: Given $H(H^+) = 1.481$ kcal mol^{-1}:
$\Delta_rH = [H(C_5H_5NH^+) - H(C_5H_5N)](627.51$ kcal mol^{-1}/h + $H(H^+)$ = _____ kcal mol^{-1}.

Δ_rH = [**(6)**_____- **(5)** _____](627.51 kcal mol^{-1}/h) + (1.481 kcal mol^{-1}] =

_____kcal mol^{-1}.
Using the literature value of -219.2 ±1.7 kcal mol^{-1}, calculate the % difference. _____