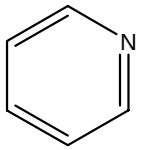
3 Choice of Theoretical Method

Exercise 1 Determine the Proton Affinity for Pyridine using AM1.



pyridine

Open / Chem3D.
Build a molecule of C_5H_5N. Use alternating entries using the Single Bond and Double Bond Tools to create C_5H_6. Click the Text Tool and click the C atom that will be changed to a N atom. Type N in the text window and hit the Enter key.
Click the Select Tool and click in the workspace.
Save as pyram1.c3d.
Calculate $\Delta_f H$ using AM1 by clicking MOPAC / Minimize Energy, selecting Theory: AM1, and Run.
Open the message window at the bottom by clicking on the Expansion Arrow and record the value _____ kcal mol^{-1}.
Save the structure.
Build the $C_5H_5NH^+$ structure by adding a H atom and placing a +1 charge on the N atom. Click the Text Tool and click the N atom. Type N+ in the text window and hit the Enter key.
Click the Select Tool and click in the workspace.
Save as hpyram1.csf. Calculate $\Delta_f H$ 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 = _____.
Close the workspace.

Exercise 2 Determine the Proton Affinity for Pyridine using PM3.

Open pyram1.c3d and save as pyrpm3.c3d.
Calculate $\Delta_f H$ using PM3 geometry. Record the value _____ kcal mol^{-1} and save the structure.
Close the workspace.
Open hpyram1.c3d and save as hpyrpm3.c3d.
Calculate $\Delta_f H$ 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 = _____.
Close the workspace.

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

Chem3D does not have *ab initio* capabilities. However, Chem3D serves as a graphical interface to Gaussian ′03 for various *ab initio* calculations and to GAMESS for Hartree-Fock *ab initio* calculations.

Using Gaussian ′03

Open pyrpm3.c3d and save as pyrdft.c3d.
Click Gaussian / Minimize Energy / Theory. Choose Method: B3LYP, Basis Set: 6-31G, Polarization: Heavy Atom d.
Click Run. (This calculation may take several minutes.) Record the value of E = _____ h.
Save the structure
Open hpyrpm3.c3d and save as hpyrdft.c3d
Calculate the minimum energy as above. Record the value of E = _____ h.
Save the structure.
Calculate the $\Delta_r H$ for

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

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

Using GAMESS

Open pyrpm3.c3d and save as pyrgam.c3d.
Click Gamess / Minimize Energy / Theory. Choose Method: Hartree-Fock, Basis Set: 6-31G, Polarization: Heavy Atom d.
Click Run. (This calculation may take a few minutes.) Record the value of E = _____ h.
Save the structure.
Open hpyrpm3.c3d and save as hpyrgam.c3d
Calculate the minimum energy as above. Record the value of E = _____ h.
Save the structure.
Calculate the $\Delta_r H$ for

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

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