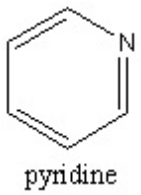
3 Choice of Theoretical Method

Exercise 1 Determine the Proton Affinity for Pyridine using MMX.



pyridine

Build a molecule of C_5H_5N by constructing a hexagon of C atoms using the draw tool. Click to periodic table tool, choose N, click on one of the C atoms, and close the periodic table. Click on the add bond tool and change every other bond to a double bond by clicking in the middle of the bonds. Click the add H tool to add the H atoms. Click Mark / Pi Atoms, choose All, and click OK. The small ~ symbols represent the conjugated π atoms.

Save as PYRMMX.pcm.

Calculate $\Delta_f H$ by selecting Compute / Minimize using MMX. Record the value _____ kcal mol^{-1} and save the structure.

Build the $C_5H_5NH^+$ structure by clicking the add H tool to remove the H atoms, clicking the periodic table tool, choosing N+, and clicking on the N atom of the C_5H_5N structure. Close the periodic table and click the add H tool.

Save as HPYRMMX.pcm. Click Compute / Minimize using MMX. 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 = _____.

Save and Close.

Exercise 2 Determine the Proton Affinity for Pyridine using Other Molecular Mechanics Methods.

Repeat the above exercise using any of the other available molecular mechanics methods available in PCModel.

Using the calculated energies and $\Delta_f H$ = 367.161 kcal mol^{-1} for H^+, calculate 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 PM3 and B3LYP/ 6-31G(d).

If GAUSSIAN or GAMESS is available, rerun the above calculations at these levels of theory, calculate the value of PA, and calculate the percent difference.