Density functional theory calculation on the pK_a values of pyridine, imidazole and pyrazole derivatives

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Abstracts

Bipyridine and its derivatives have been widely used as the ligands in transition metal complexes. Ruthenium polypyridine (bipyridine and terpyridine) complexes have received extensive attention due to their strong metal to ligand charge-transfer transitions, facile electron-transfer properties and long lived 3MLCT excited states and these in combination make them attractive for designing photo- and electrochemical devices. The proton affinities of polypyridine were calculated using an *ab initio* quantum mechanical method (B3LYP with various double zeta and triple zeta basis sets) in combination with the Poisson-Boltzmann continuum solvation model. Vdw radii of the atoms in the heterocyclic rings for the solvation energy calculation were set to according to guanine and oxyguanine and that of chlorine was optimized to reproduce the experimental values of relating compounds. The p*K*a values for the heterocyclic ring compounds were in agreement with the experimental values with a mean unsigned error of 0.45 pK_a units.

pK_a

Definition of pK_a

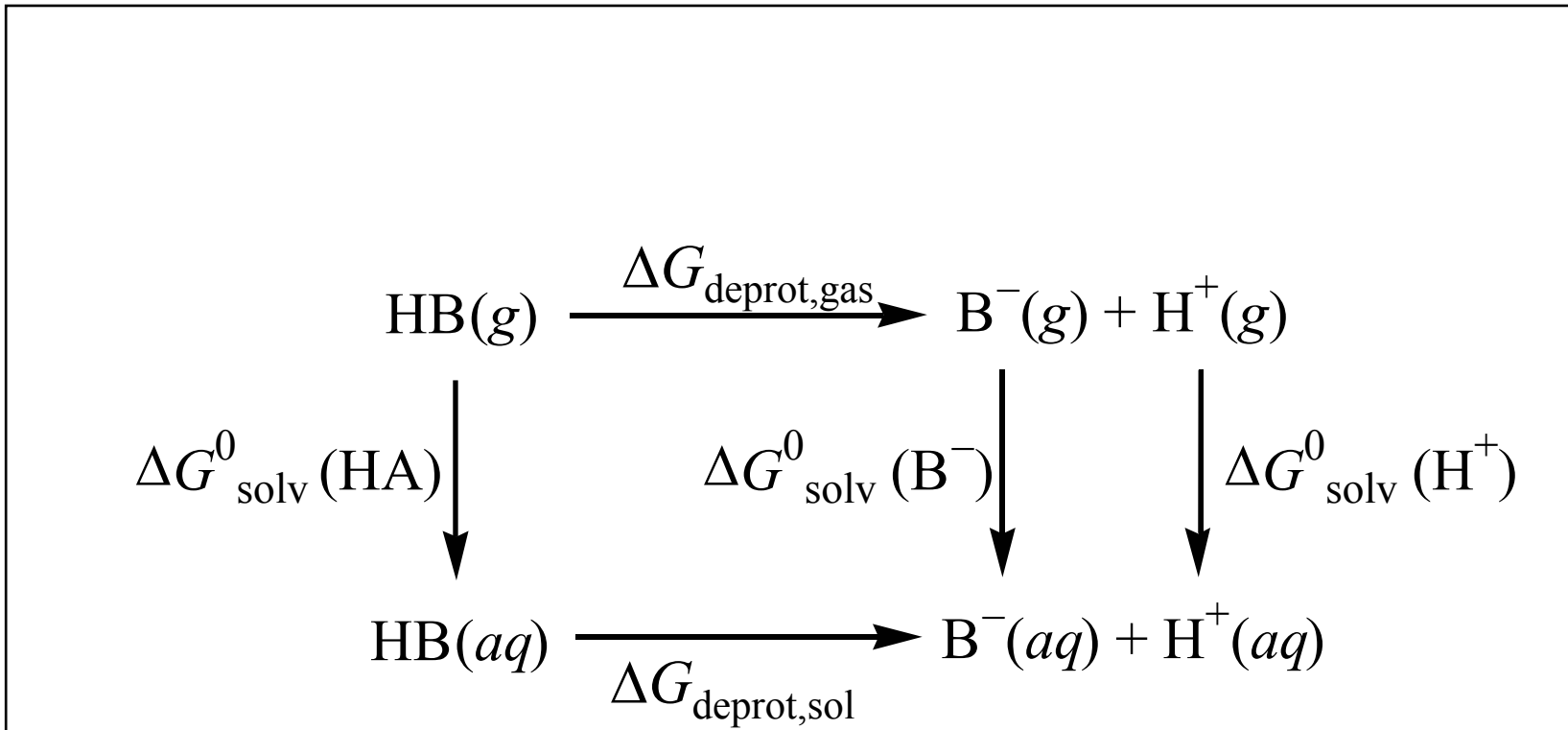
- $HB(sol) \rightleftarrows H^+(sol) + B^-(sol)$

$$K_a = \frac{[H^+][B^-]}{[HB]}$$

$$\Delta G_{deprot,sol} = \Delta G(H^+, sol) + \Delta G(B^-, sol) - \Delta G(HB, sol)$$
$$= -RT\ln K_a$$

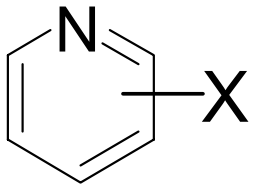
$$pK_a = -\log K_a = \frac{1}{2.303RT}\Delta G_{deprot,sol}$$

Thermodynamic cycle for the deprotonation

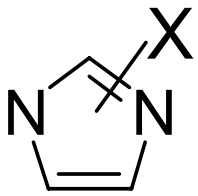


Model compounds

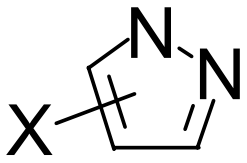
pyridine, imidazole, and pyrazole derivatives



X = H (**1**), 2-Cl (**6**), 3-Cl (**7**), 4-Cl (**8**)
2-CH_3 (**10**), 3-CH_3 (**12**), 4-CH_3 (**15**)



X = H (**2**), 1-CH_3 (**14**), 2-CH_3 (**4**), 4-CH_3 (**5**)

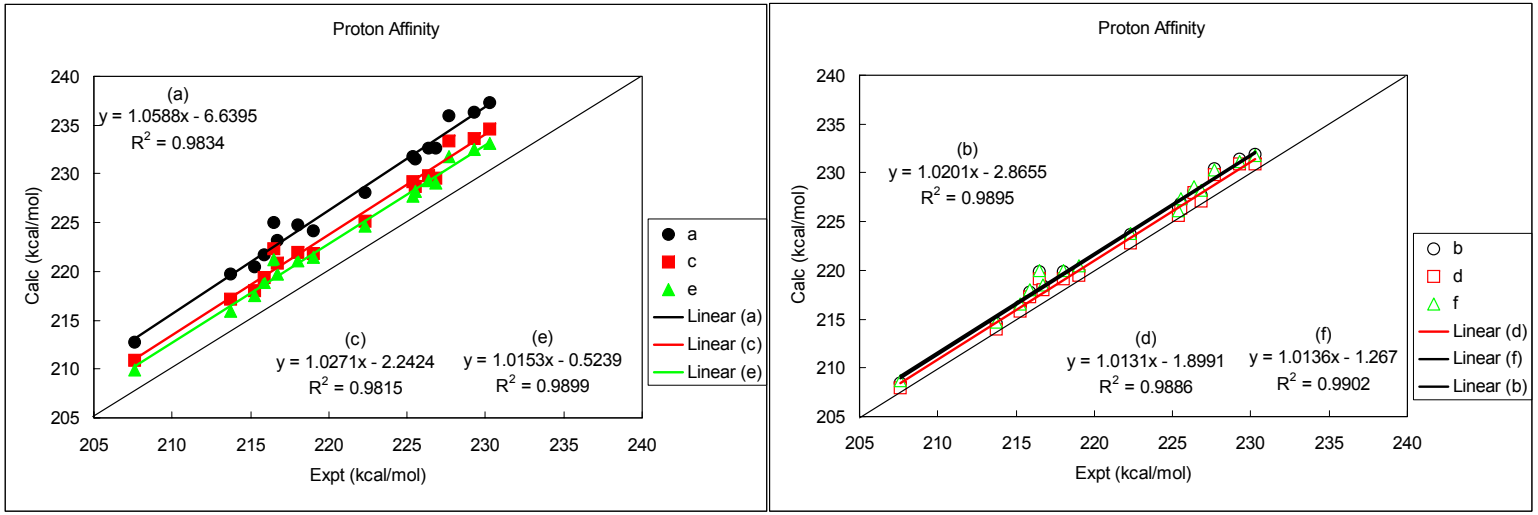


X = H (**3**), 1-CH_3 (**16**), 3-CH_3 (**9**),
4-CH_3 (**11**), 4-Cl (**13**)

Choosing level of theory

Proton affinity

$$\Delta H_g^0(\mathrm{A}^-) + \Delta H_g^0(\mathrm{H}^+) - \Delta H_g^0(\mathrm{HA})$$

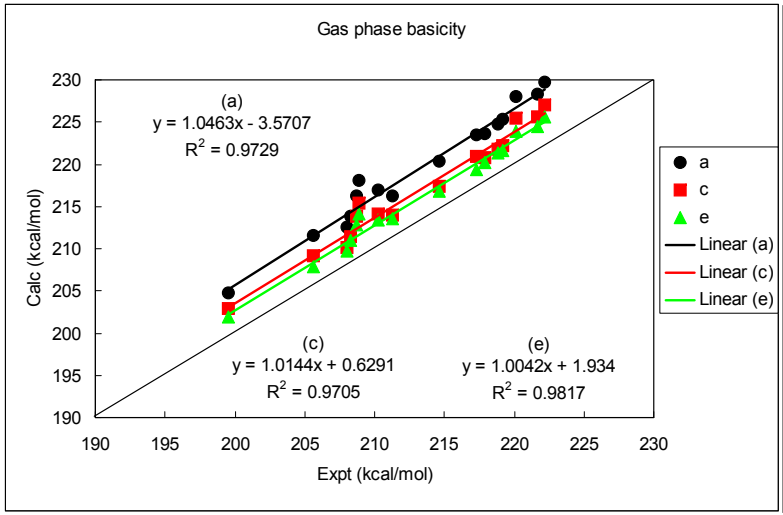


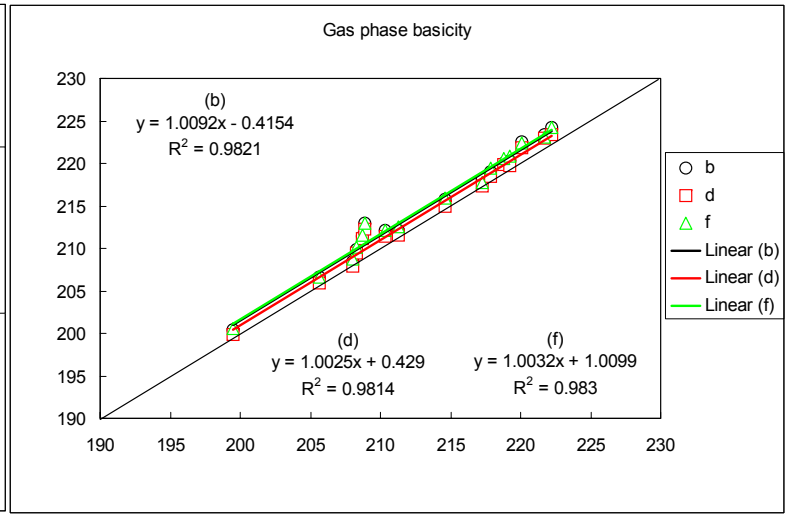
d: cc-PVDZ++

Choosing level of theory

Gas-phase basicity

$$\Delta G_g^0(\mathrm{A}^-) + \Delta G_g^0(\mathrm{H}^+) - \Delta G_g^0(\mathrm{HA})$$



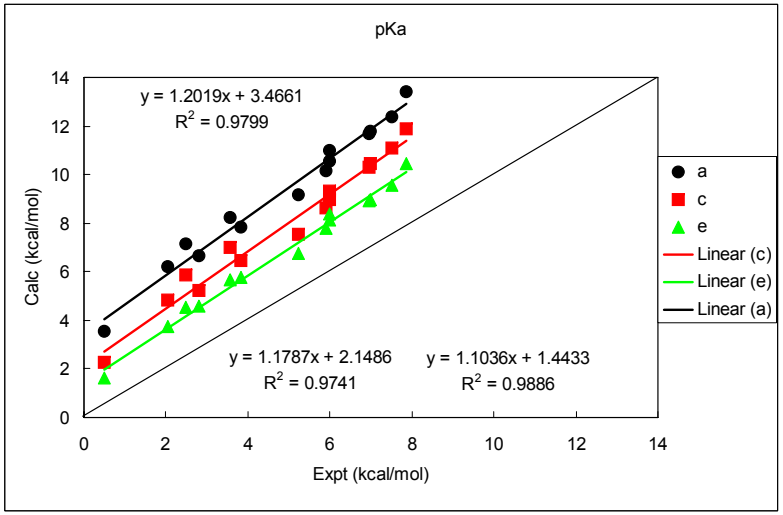


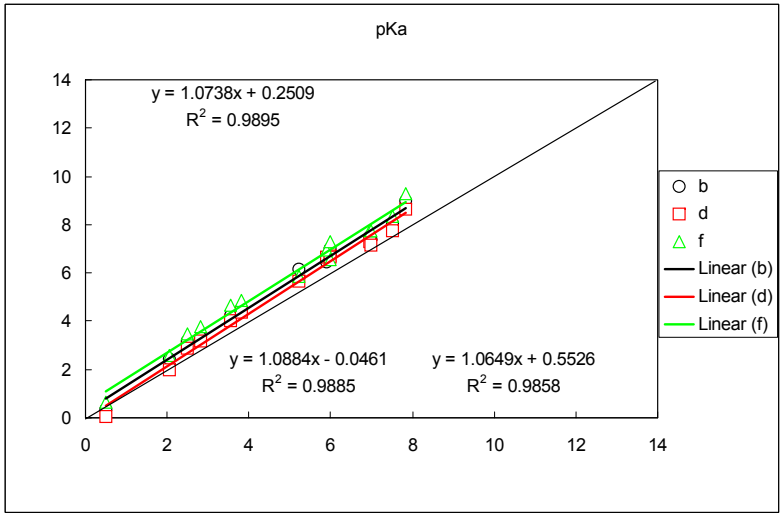
d: cc-PVDZ++

Choosing level of theory

pK_a

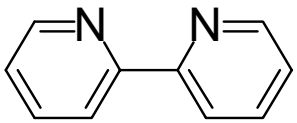
$$\frac{1}{2.303RT}\Delta G^0_{deprot,aq}$$



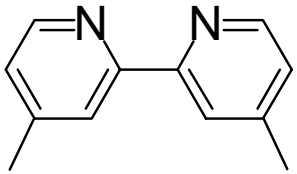


d: cc-PVDZ++

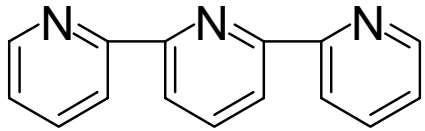
Bipyridine, terpyridine



$pK_a = 5.52$



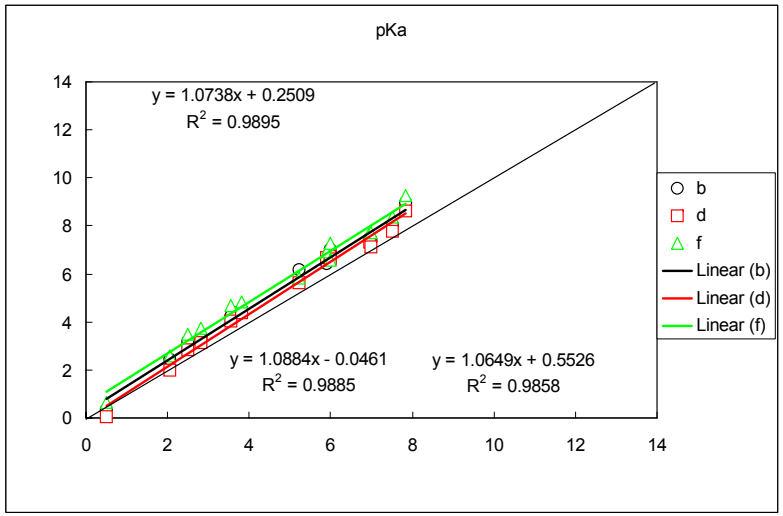
$pK_a = 6.24$



$pK_a = 4.51$

Summary

- pK_a values for pyridine, imidazole, and pyrazole derivatives
- Excellent agreements with the experiments



- Further works
  - conformations, isomers
  - transition metal complexes