DEA TO ADENINE & CO : RESULTS FROM QUANTUM CHEMISTRY

NATCHA INJAN

Permanent address:
Kasetsart University, Bangkok

Original motivation

- Experimental results from Stephan Denifl from the Märk / Scheier group
- Dissociative electron attachment to purine derivatives (adenine …)
- An interesting spectrum of the $[M-H]^-$ count as function of the electron energy is measured.
- The spectrum is reminiscent of the one in thymine and uracil.

Background

- Radiation damage to DNA (contains adenine) and RNA.
- General interest in mechanism of electron-molecule reactions.

Suggested mechanism

- An electron is captured in a dipole – bound state.
- It enters an antibonding σ^* orbital to form a metastable anion that can weaken a N-H (or C-H) bond.
- H can dissociate and $[M\text{-}H]^-$ remains.

What we worked on …

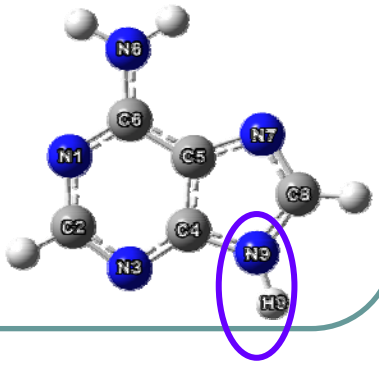
1. Which H dissociates most easily ?
   (calculations of BDE)
2. Neutral and anionic energy surface – where do they cross ?
   (calculation of stable and metastable potential energy curves)
3. Why do the purine derivatives show different spectra ?
   (analysis of molecular orbitals)

1. Which H dissociates most easily ?

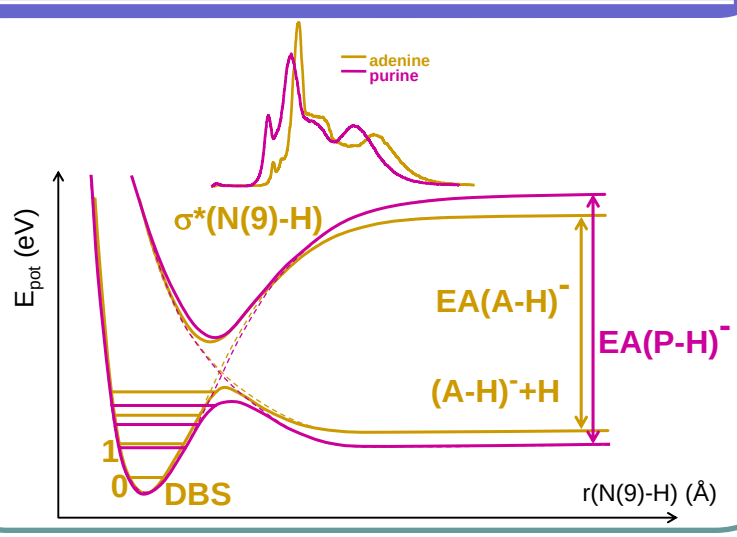
Experimental finding: H(N9)

QC calculations (G2(MP2) on adenine):

BDE of H from	System neutral	anion
C2	4.74	3.63
N6	4.69	1.72
C8	5.06	2.53
N9	4.38	0.94



2. Neutral and anionic energy surface Paul Scheier's schematic picture:

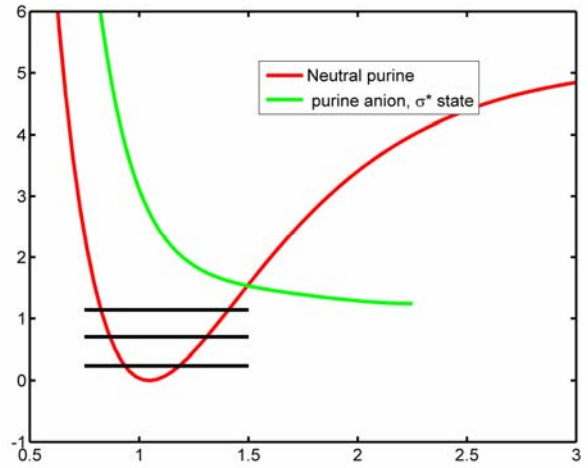


2. Neutral and anionic energy surface

Can we calculate these curves ?

- Neutral curve: **YES**
- Stable part of the anionic curve:
  (excited state but below neutral curve)
  YES
- Metastable part of the anionic curve
  (above neutral): ~~**NO**~~ **YES**
  We implemented an extrapolation method for the metastable energy
- Avoided crossing: **NO**
  (has never been done, difficult …)

2. Neutral and anionic energy surface



2. Neutral and anionic energy surface

In principle, the probability of

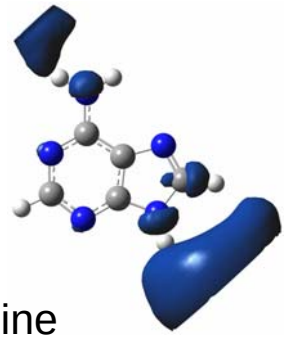
$M + e^- \rightarrow [M\text{-}H]^- + H$

can be calculated from these curves !

(via tunneling rates;
the accuracy is a problem)

3. Why do the purine derivatives show different spectra ?

Electron distribution in σ* - MO of adenine:

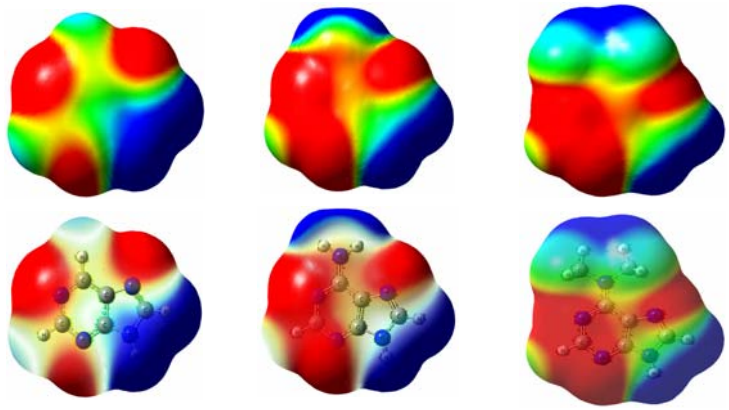


- Similar in dimethyladenine
- In purine ‘upper part’ is absent !

•Why ?

3. Why do the purine derivatives show different spectra ?

Because of the ESP (Electrostatic potential):
red=negative, blue=positive



Purine Adenine Dimethyladenine

Concluding …

- Some (not all) features could indeed be explained !