

Abstract

Potential energy curves for pyridine (along C-H bond) and 2-bromopyrazine (along C-Br bond) are reported, providing a rough description of a dissociative electron attachment process studied with a simple density functional theory approach. Vertical electron attachment energies for pyridine, pyrazine and their halo derivatives are also presented.

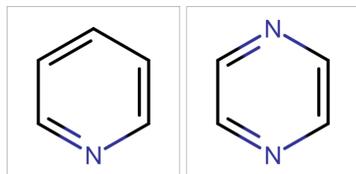


Figure 1: Structural formulas of pyridine and pyrazine.

Vertical electron affinities

Vertical electron affinities (VEAs) were obtained as the energy difference between neutral and anion ground state, both in optimized neutral geometry. VEAs with various basis sets for pyridines compared with available experimental data [1] are shown in Figure 2. As readily seen, the MP2 method either considerably underestimates the results or predicts the wrong anion state. Unfortunately, the problem also arises for DFT with increasing basis set, with the pyridine molecule apparently being the most sensitive for those changes. One can notice, that although B3LYP/aug-cc-pVTZ gives the closest results to the experimental values, they are only slightly improved compared to those obtained at 6-31+G* and 6-311++G** level. All calculations in this work were performed with Gaussian 16 program suite [2].

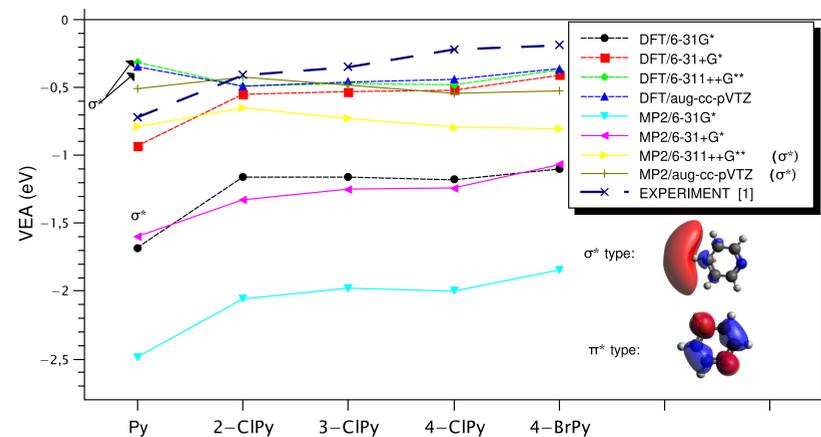


Figure 2: The lowest in energy VEAs obtained at given basis set, with an indication of which of them relate to σ^* states. It should be noted that all the results obtained with MP2/6-311++G** and aug-cc-pVTZ basis sets concern σ^* states.

Potential energy curves

Relaxed and symmetry-constrained potential energy curves (PECs) for 2-bromopyrazine and pyridine are shown in Figure 3. A similar analysis has been carried out earlier by Sanche and coworkers, see e.g. [3]. For each molecule, four different curves along C_n-X bond are investigated, namely the one of the neutral molecule, relaxed anionic curve (representing π^*/σ^* mixed state), π^* planar state, and pure σ^* state. Further analysis of Mulliken charges and spins suggests that the most energetically favored process for pyridine and pyrazine is the one described with the following equation:



while in substituted molecules the electron rather stays at halogen atom:



for X=Cl, Br, where e_0^- stands for thermal electron (≈ 0 eV). In both cases the anionic lowest (ground) state passes from π^* - to σ^* -type SOMO (singly occupied molecular orbital) and therefore the molecule must undergo a symmetry change during the process. Activation energy values (E_0) for pyridine derivatives show that the lowest anion state is almost repulsive along C-X bond, whereas for halo pyrazines they have a slightly higher values. It should be noted that all pyridines with an excess electron are not stable systems and they are bound artificially. Moreover, in such studies time dependence of reaction dynamics is not taken into account. The summary of the results is presented in Table 1.

Potential energy curves

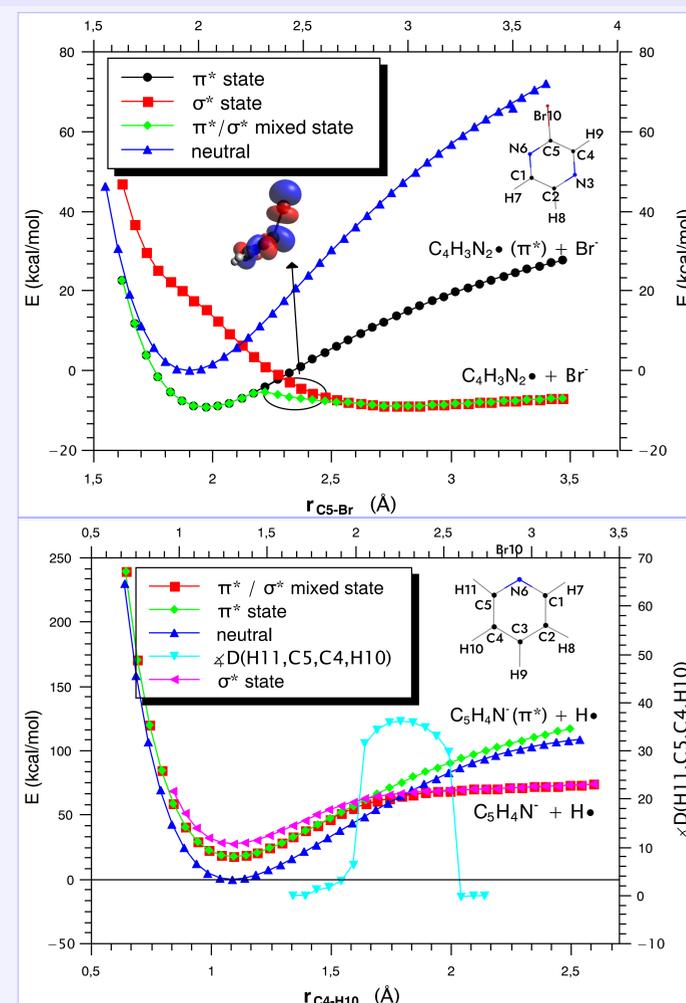


Figure 3: Example adiabatic potential energy curves along indicated bonds for 2-bromopyrazine (upper) and pyridine (lower).

	VEA ^a (eV)	VEA (lit. ^b , eV)	E ₀ ^c (kcal/mol)	ΔH ^{a,d} (eV)
(1)	-0.85	-0.72	-	3.26-3.68 ^e
2-Cl(1)	-0.48	-0.41	1.38	≈ 0
2-Br(1)	-0.42	-	≈ 0	-0.40
3-Cl(1)	-0.46	-0.35	1.18	2.29
3-Br(1)	-0.40	-	≈ 0	1.91
4-Cl(1)	-0.44	-0.22	≈ 0	0.13
4-Br(1)	-0.36	-0.19	≈ 0	-0.26
(2)	-0.22	-0.08	-	3.32
2-Cl(2)	0.14	-	5.78	-0.03
2-Br(2)	0.2	-	3.79	-0.42

Table 1: Quantities calculated for pyridine (1), pyrazine (2) and derivatives at ^aB3LYP/aug-cc-pVTZ level, ^bB3LYP/6-31+G* level of theory. ^cResults taken from [1]. ^dEnthalpies of reactions of type 1 for pyridine and pyrazine and reactions of type 2 for substituted molecules. ^eCalculated for 3-,4- and 5- hydrogen position, from the lowest to highest value, respectively.

Acknowledgements

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References

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