

A DFT STUDY OF DISSOCIATIVE ELECTRON ATTACHMENT TO C₅XH₄N AND C₄XH₃N₂ (X=H,Cl,Br) AROMATIC MOLECULES

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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.

1. INTRODUCTION

Of the many possible electron-molecule interaction processes, dissociative electron attachment (DEA) is one of the most interesting, albeit still not fully described and understood. In this work, we examine the interaction of low-energy electrons with pyridine, pyrazine, and their halo derivatives with a simple density functional theory approach, as well as the applicability of this method to anions in comparison to second order Moller-Plesset perturbation theory (MP2). Pyridine and pyrazine are only briefly discussed in the literature in the context of cross sections for electron scattering [Szymtkowski *et al.*, 2019, Sanz *et al.*, 2013], or temporary anions [Nenner & Schultz 1975, Mathur & Hasted, 1976]. For 2- and 3-bromopyridine and halopyrazines vertical electron attachment energies are reported for the first time.

1. 1. CALCULATIONAL APPROACH

Various parameters of neutral and anion ground states of studied targets in the gas phase have been calculated using the DFT with B3LYP functional and MP2 methods with 6-31G*, 6-31+G*, 6-311++G**, and aug-cc-pVTZ basis sets. Vertical electron attachment energy (VEA) was obtained as the energy difference between neutral and anion ground state, both in optimized neutral geometry. Enthalpies for the following reactions are also evaluated and reported:



for non-substituted hydrocarbons and



for X=Cl, Br, where e_0^- stands for thermal electron (0 eV). Furthermore, the adiabatic potential energy curves, from which the activation energy can be read, obtained in 6-31+G* basis set with B3LYP functional for dissociative processes are presented and discussed. All calculations were performed with Gaussian 16 program suite.

2. RESULTS AND DISCUSSION

2. 1. VERTICAL ELECTRON ATTACHMENT ENERGIES

Calculated VEAs with various basis sets for pyridines compared with available experimental data 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. Moreover, this problem also concerns to pyrazine and its derivatives (not shown). 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. This has also been confirmed for other molecules, as well as better performance than MP2 if diffuse functions are included [Szarka *et al.* 1998]. 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. According to DFT calculations, the lowest state of pyrazine anion (${}^2B_{3u}$) is bound (with ZPE correction) and so are anions of its derivatives, in contrary to pyridine-like molecules, however the VEA of pyrazine is confirmed to be negative. Values of VEA and ΔH obtained at B3LYP/aug-cc-pVTZ level (and estimated as the best) are listed in Table 1 and 2.

	(1)	2-Cl(1)	2-Br(1)	3-Cl(1)	3-Br(1)	4-Cl(1)	4-Br(1)
VEA (eV)	-0.85	-0.48	-0.42	-0.46	-0.4	-0.44	-0.36
VEA ^a (lit., eV)	-0.72	-0.41	-	-0.35	-	-0.22	-0.19
E_0 (kcal/mol)	-	1.38	≈ 0	1.18	≈ 0	≈ 0	≈ 0
ΔH (eV)	3.26-3.68 ^b	≈ 0	-0.40	2.29	1.91	0.13	-0.26

Table 1: E_0 calculated with B3LYP/6-31+G*, ΔH from Eq. (1-2) and VEA, both calculated at B3LYP/aug-cc-pVTZ level for pyridine (1) and halo derivatives.

^aExperimental results of Nenner & Schultz, 1975. ^bCalculated for 3-,4- and 5-hydrogen position, from the lowest to highest value, respectively.

	(2)	2-Cl(2)	2-Br(2)
VEA (eV)	-0.22	0.14	0.2
VEA (lit., eV)	-0.08 ^c	-	-
E_0 (kcal/mol)	-	5.78	3.79
ΔH (eV)	3.32	-0.03	-0.42

Table 2: Calculated and literature values for pyrazine (2) and halo derivatives, see Table 1 for further explanation. ^cMathur & Hasted, 1976.

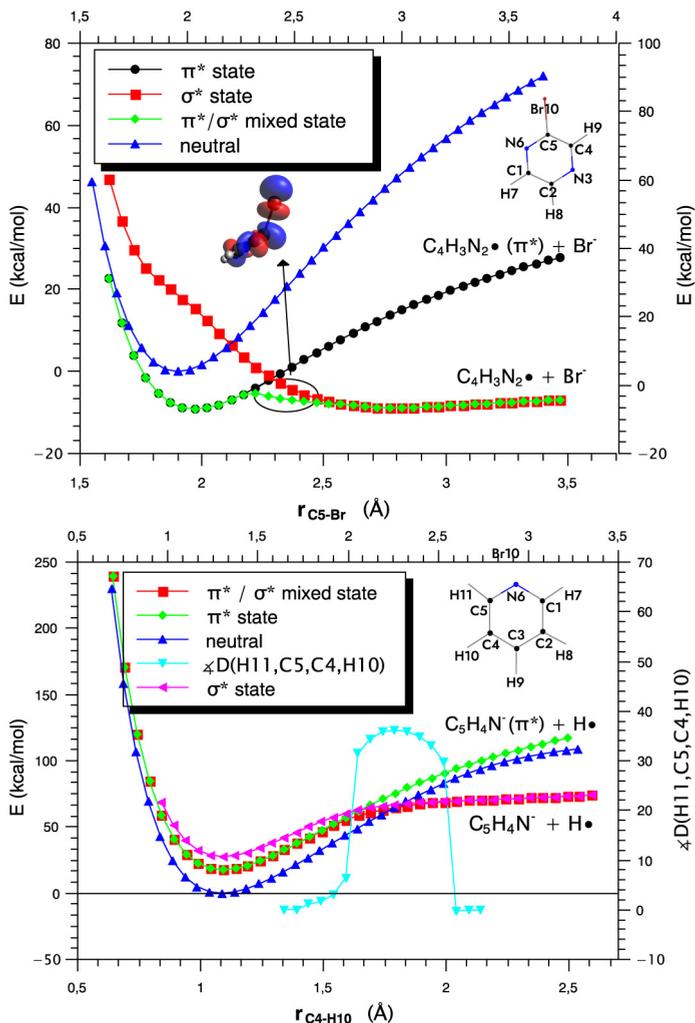


Figure 1: Example adiabatic potential energy curves along indicated bonds for 2-bromopyrazine (upper) and pyridine (lower).

2. 2. ADIABATIC POTENTIAL ENERGY CURVES

Potential energy curves (PECs) for 2-bromopyrazine and pyridine are shown in Figure 1. A similar analysis has been carried out earlier [e.g. Li, Sanche & Sevilla, 2002 and other works of these authors]. 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 Eq. 1, while for substituted molecules with Eq. 2, with the anionic lowest (ground) state in both cases passing from π^* - to σ^* -type SOMO (singly occupied molecular orbital). During such

a process, the molecule must undergo a symmetry change [e.g. Modelli & Venuti, 2001], which reveals in a rapid change of dihedral angle containing X atom. This reaction is recognized as the electron transfer process. Similar PECs were obtained for the rest of molecules of interest. 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.

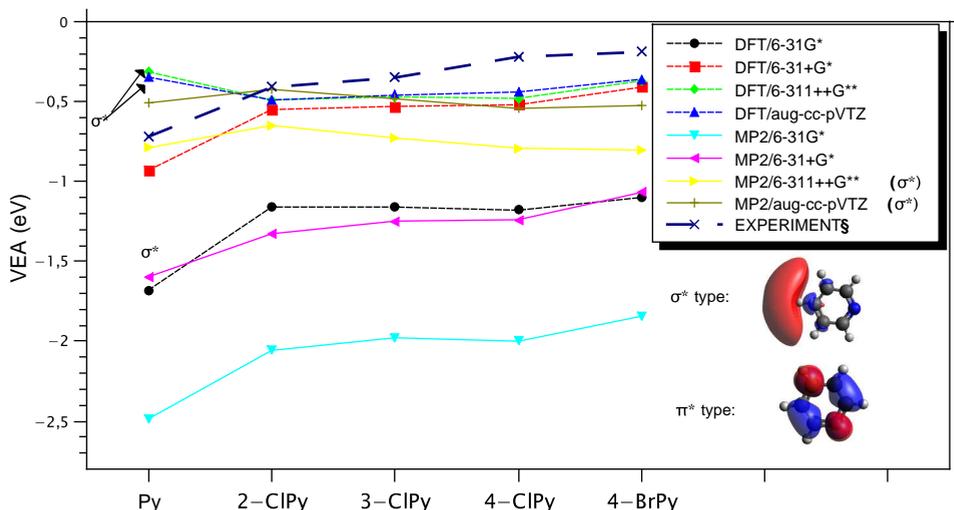


Figure 2: § Nenner & Schultz 1975. The lowest in energy VEAs obtained at given basis set, with an indication of which of them relate to σ^* states. It should be noted that all the results obtained with MP2/6-311++G** and aug-cc-pVTZ basis sets concern σ^* states.

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