

# Supplementary material

## Crystallographic and *ab initio* Study of Pyridine Stacking Interactions. Local Nature of Hydrogen Bond Effect in Stacking Interactions. Supplementary material

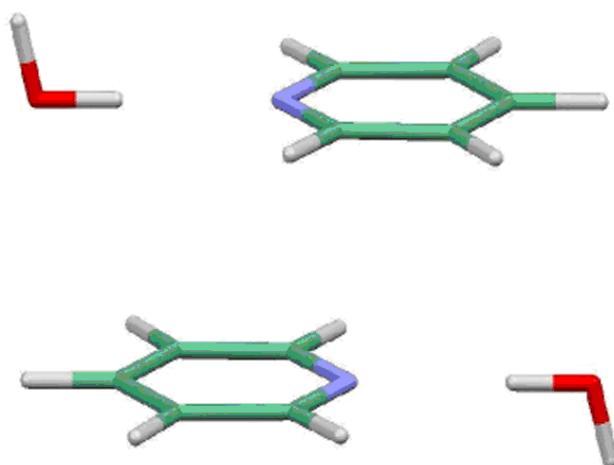
Dragan B. Ninković, Goran V. Janjić<sup>†</sup> and Snežana D. Zarić <sup>††\*</sup>

### I Energy of stacking interactions between pyridine-water dimers with optimized geometry

To study influence of hydrogen bonds on pyridine-pyridine stacking interactions, model systems with pyridine-water (**pw**) dimers were used. The interaction energy of hydrogen bond between water and pyridine has been calculated for the mutual perpendicular orientation of molecules. We present here the data for nonoptimized (the same data are presented in the main text of the paper), and for optimized pyridine-water dimer. The geometry of nonoptimized pyridine-water dimer with the strongest of hydrogen bond was calculated for the mutual perpendicular orientation of two molecules by changing the distance between pyridine nitrogen and water hydrogen. The geometry with lowest energy had H···N distance of 2.0 Å and binding energy ( $\Delta E_{\text{pyr...HOH}}$ ) of -5.90 kcal/mol (MP2/6-311++G\*\*) (Table S1).

This geometry was used as starting geometry for pyridine-water dimer optimization. The optimization was done using the 6-311++G\*\* basis set and Møller-Plesset second-order perturbation method (MP2). During optimization the geometry of pyridine molecule did not change, while small changes in geometry of water molecule occurred (Table S1). The changes are observed in the length of O-H bonds, in the length of H···N distance and in angle of hydrogen bond (O-H···N angle). These changes did not have significant influence on the energy of hydrogen bond; the energy of hydrogen bond ( $\Delta E_{\text{pyr}\cdots\text{HOH}}$ ) in optimized pyridine-water dimer is -6.10 kcal/mol (Table S1).

The energy of stacking interactions between two pyridine-water dimers was calculated for nonoptimized and for optimized dimers (Table S1). The optimal geometry for stacking interaction was obtained by shifting the center of one pyridine molecule along the N···O···C line of second one, while the geometry of pyridine-water dimer was kept rigid. For various offset values, we changed normal distances and found the structures with the lowest energy. The strongest interactions energy was obtained for offset of -1.80 Å, both for nonoptimized and for optimized pyridine-water dimer. The calculated energies of the stacking interaction are similar, -6.86 and -6.84 kcal/mol, for nonoptimized and optimized pyridine-water dimers, respectively.



**Figure 1.** Schematic view of stacking interaction geometry of pyridine-water dimer.

Table S1. Geometric data and interaction energies for pridine-water (**pw**) dimer.

	<b>Before optimisation*</b>	<b>After optimisation*</b>
<b>r (Å)</b>	-1.80	-1.80
<b>R (Å)</b>	3.25	3.25
<b>d(O-H) (Å)</b>	0.96	0.97
<b>d(H··N) (Å)</b>	2.00	2.02
<b>O-H··N angle (°)</b>	180.0	177.4
<b><math>\Delta E_{pyr\cdots HOH}</math> (kcal/mol)</b>	5.90	6.10
<b><math>\Delta E_{pw  pw}</math> (kcal/mol)</b>	6.86	6.84

\*optimization of pyridine-water (**pw**) dimer

## II Correlation energies of stacking interactions between pyridine-pyridine and pyridine-water dimers

Table S2. Calculated energies of stacking interactions at HF/6-311++G\*\* and MP2/6-311++G\*\* levels, and correlation energy for pyridine-pyridine (pyr||pyr) and pyridine-water (pw||pw) dimers.

	<b>r</b>	<b>ΔE<sub>HF</sub></b>	<b>ΔE<sub>MP2</sub></b>	<b>ΔE<sub>CORR</sub><sup>a</sup></b>
<b>pw  pw</b>	-1.8	2.06	-6.86	-8.92
<b>pyr  pyr</b>		5.04	-2.67	-7.71
<b>pw  pw</b>	1.3	2.78	-4.88	-7.66
<b>pyr  pyr</b>		3.46	-4.08	-7.54

<sup>a</sup>  $\Delta E_{\text{CORR}} = \Delta E_{\text{HF}} - \Delta E_{\text{MP2}}$