Supplementary Information

Crystallographic and *ab initio* Study of Pyridine CH/O Interactions. Linearity of the interactions and influence of pyridine classical hydrogen bonds

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1. Analysis of the data from CSD for non-substituted pyridines

The structures from CSD were screened for CH/O interactions between pyridine and water with H⋯O distances shorter than 2.9 Å and C-H⋯O angles larger than 110°. This rigorous criteria was used to avoid at least the shortest C-H⋯H-O van der Waals contacts and parallel alignment interactions. Using this criteria, we found only 9 CH/O contacts. To obtain large number of contacts, criterion for H⋯O distances has been extended (d < 3.2 Å). In this search we found 15 contacts, and in almost all contacts (13), pyridine N atom simultaneously forms classical hydrogen bond. By visual analysis of the structures, with H⋯O distances shorter than 3.2 Å, we have concluded that in these structures there are no short C-H⋯H-O contacts and parallel alignment interactions.

In spite of relatively small number of CH/O contacts (15), some trends can be observed. The distribution of distance d for nonsubstituted pyridines is shown in Fig. S1. It shows no clear preference as there are two pronounced peaks in ranges 2.5-2.6 Å and 2.9-3.0 Å. However, most of the interactions are formed with H⋯O distances above 2.5 Å.

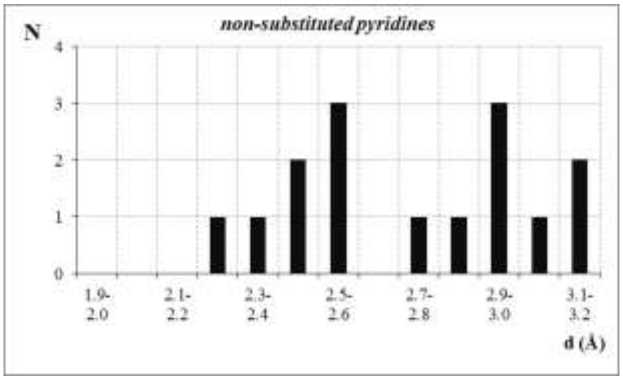
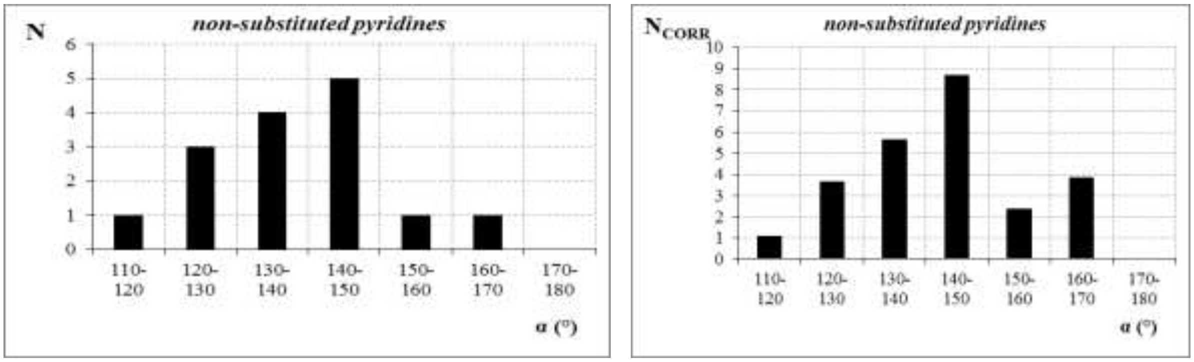


Fig. S1. Distributions of d distance for CH/O interactions between non-substituted pyridine molecule and water molecule.

The distributions of angle α, both non-corrected and corrected are presented in Fig. S2. It is interesting that both distributions show that there is no preference for linear interactions, although number of analyzed structures is rather small.



(a) (b)

Fig. S2. Distributions of angle α: Noncorrected (a) and cone-corrected (b) for pyridine-water CH/O interactions of non-substituted pyridines.

In order to study the preference of CH/O interactions for linear or bifurcated geometries, we analyzed the distribution of the angle φ (Methodology, Fig. 1). The peaks of angle φ in the regions of 80-90° and 150-160° are consequence of the bifurcated CH/O interactions. Depending on the type of two neighboring hydrogen atoms of the aromatic ring, included in bifurcated interacion, the peaks are more or less pronounced. The peak in the region of 150-160° is most pronounced and corresponds to bifurcated CH/O interactions, involving the *meta* and *para* CH groups of pyridine. The peak, for interactions that involve the *ortho* and *meta* CH groups, is less pronounced.

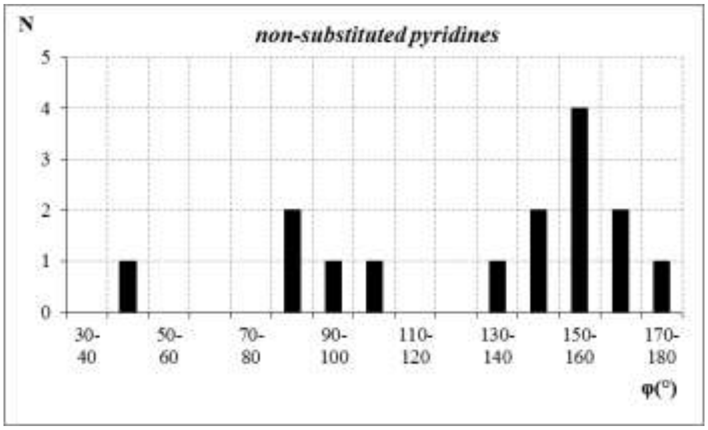


Fig. S3. Distributions of angle φ for CH/O interactions between non-substituted pyridine molecule and water molecule.

2. Visual analysis

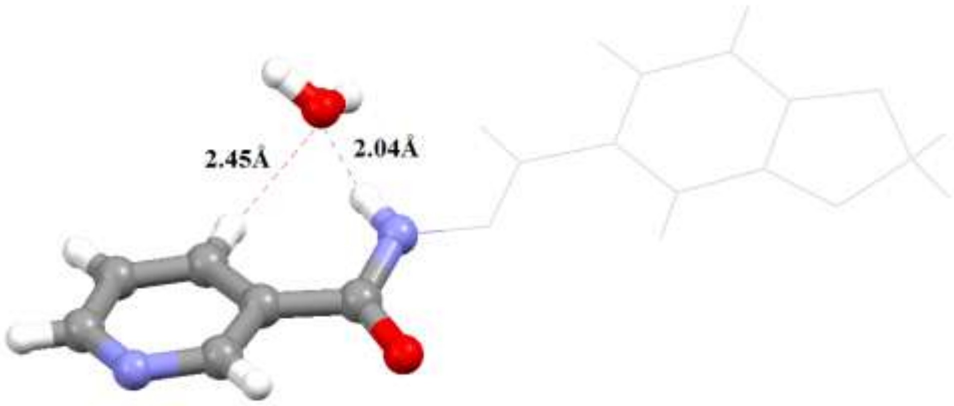


Fig. S4. View of BUDNIY[S1] crystal structure ((E)-N'-(1,3-Benzodioxol-5-ylmethylene)-nicotinohydrazide monohydrate) where water oxygen atom simultaneously form CH/O interaction (red line) with *para* C-H group of pyridine fragement (d(H···O)=2.45 Å and α(C-H···O)= 156.1°) and classical hydrogen bond (blue line) with N-H group of substituent fragment (d(H···O)=2.05 Å and α(N-H···O)= 164.1°).

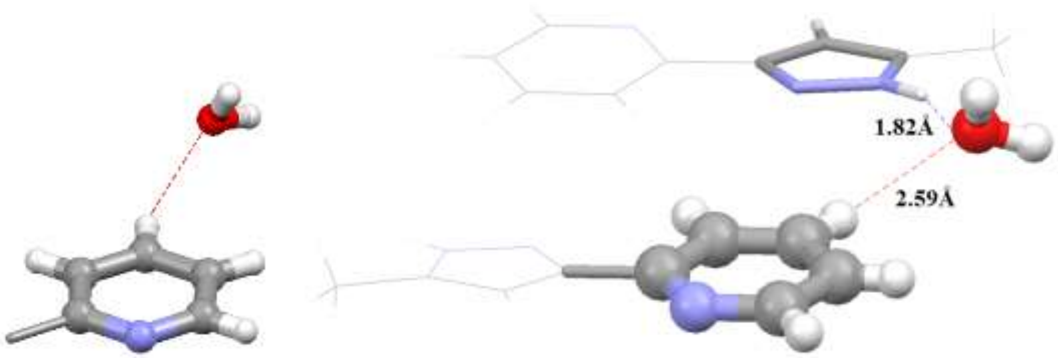


Fig. S5. Two views of ALACAR[S2] crystal structure (5-methyl-3-(pyrid-2-yl)-1H-pyrazole monohydrate) where water oxygen atom simultaneously forms bent CH/O interactions (red lines) with *para* C-H group of pyridine fragment (d(H···O)=2.59 Å and α(C-H···O)= 142.4°) and classical hydrogen bond (blue line) with N-H group of pyrazole fragment (d(H···O)=1.82 Å and α(N-H···O)= 142.4°).

3. NPA analysis

Results of the NPA analysis confirmed that there is a charge transfer from pyridine to water molecule of 13 me when they form a hydrogen bond. The consequence of this charge transfer is that the charge of pyridine molecule is +0.13me which is possible explanation for the strengthening the CH/O interactions. The increase of the partial charge of hydrogen atoms affects the *ortho* H atoms to the largest extent, followed by *meta* and *para* H atoms the least (Fig. S6). In comparison to the values of partial charges of pyridine molecule (without hydrogen bond) the increase of partial charges are 3.5% for *ortho*, 1.9% for *meta* and 1.4% for *para* H atoms. The increase in strength of CH/O interactions is 32.2% for *ortho*, 20.6% for *meta* and 18.3% for *para* set). Trend of the strengthening interactions is the same as the trend of the increase of partial charges of hydrogen atoms in pyridine molecule with hydrogen bond (Table S1).

Table S1. Results of the NPA analysis and CH/O interaction energies for pyridine without and with hydrogen bond.

Model system	Pyr	W/Pyr	$PyrW_{H\text{-bond}}$	$W/PyrW_{H\text{-bond}}$	$\Delta\Delta E^a$		$\Delta\delta_H^b$	
	δ_H (me)	ΔE (kcal/mol)	δ_H (me)	ΔE (kcal/mol)	(kcal/mol)	%[c]	(me)	%[c]
Ortho	181.25	-1.24	187.52	-1.64	-0.40	32.3	6.27	3.5
Meta	206.46	-1.94	210.33	-2.34	-0.40	20.6	3.87	1.9
Para	203.14	-1.97	205.98	-2.33	-0.36	18.3	2.84	1.4

[a] $\Delta\Delta E = \Delta E_{[W/PyrWH\text{-bond}]} - \Delta E_{[W/Pyr]}$

[b] $\Delta\delta_H = \Delta\delta_{H\,[W/PyrWH\text{-bond}]} - \Delta\delta_{H\,[W/Pyr]}$

[c] percentage of change in partial charge for pyridine with hydrogen bond

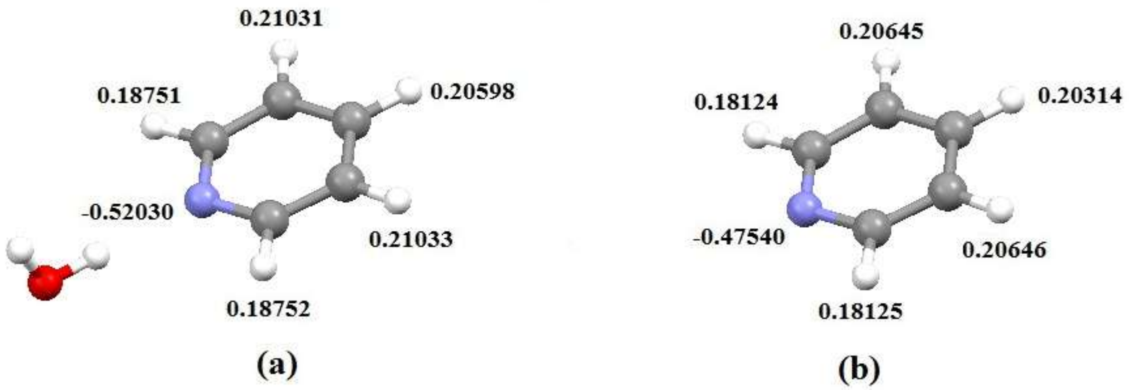


Fig. S6. Calculated partial charges of nitrogen and hydrogen atoms in hydrogen bonded water-pyridine system (a) and of pyridine molecule (b).

Table S2. Results of the NPA analysis for pyridine and pyridine with hydrogen bond systems.

Model system	Pyr	W/Pyr	Δq (me)
	δ_H (me)	ΔE (kcal/mol)	
Ortho	181.25	-1.24	2.08
Meta	206.46	-1.94	2.83
Para	203.14	-1.97	2.87

4. The influence of diffuse functions in the basis set

To estimate the influence of diffuse functions in the basis set, we performed additional single point calculations including diffuse functions (aug-cc-pVTZ basis set) on system with monofurcated CH/O interactions. The results of calculations showed that the introduction of diffuse functions leads to slightly increasing of the interaction energy (less than 0.1 kcal/mol) (Table S3).

Table S3. Calculated MP2 interaction energies (in kcal/mol) with two types of basis set

Level of calculations	Ortho	Meta	Para
MP2/cc-pVTZ	-1.16	-1.84	-1.87
MP2/aug-cc-pVTZ	-1.23	-1.92	-1.95

References:

S1. Feng-Yu Bao, Hai-Yan Zhang, Ying-Xia Zhou, Su Hui, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2009, **65**, 2331.
S2. Wei-Shan Yu, Chung-Chih Cheng, Yi-Ming Cheng, Pei-Chi Wu, Yi-Hwa Song, YunChi, Pi-Tai Chou, *J. Am. Chem. Soc.*, 2003, **125**, 10800.