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Supplementary Material (SI)

Influence of hydrogen bonds on edge-to-face interactions between pyridine molecules

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S1. Calculation of interactions energy in edge-to-face interactions between two pyridine molecules

The interaction energy between two pyridine molecules, $\Delta E_{(Pd\perp Pa)}$, was defined as difference of energy of dimer molecule and energies of monomers. In the symbol ($P_d \perp P_a$), P_d denotes the donor-pyridine molecule; symbol P_a denotes the acceptor pyridine molecule, while the symbol $\perp$ denotes edge to face orientation of molecules.

$$\Delta E\ (Pd \perp Pa) = E_{PdPa} - E_{Pd} - E_{Pa} \quad (1)$$

The energy of edge to face interaction, between two pyridine molecules with hydrogen bonds in $W1^{\cdots}P_d \perp P_a$ and $P_d \perp P_a{}^{\cdots}W2$systems (W1 is water molecule that forms hydrogen bond with donor-pyridine, while W2 is water molecule that forms hydrogen bond with acceptor pyridine) was calculated for binary system using the equations 2 and 3.

$$\Delta E\ (W1 \cdots Pd \perp Pa) = E_{W1PdPa} - E_{W1Pd} - E_{Pa} \quad (2)$$

$$\Delta E\ (Pd \perp Pa \cdots W2) = E_{PdPaW2} - E_{Pd} - E_{PaW2} \quad (3)$$

The change of strength of edge-to-face interactions between two pyridine molecules in systems with hydrogen bonds ($W1^{\cdots}P_d \perp P_a$ or $P_d \perp P_a{}^{\cdots}W2$) and without hydrogen bond ($P_d \perp P_a$) is expressed by $\Delta\Delta E$ (the equation 4 and 5).

$$\Delta\Delta E = \Delta E\ (W1 \cdots Pd \perp Pa) - \Delta E\ (Pd \perp Pa) \quad (4)$$

$$\Delta\Delta E = \Delta E\ (Pd \perp Pa \cdots W2) - \Delta E\ (Pd \perp Pa) \quad (5)$$

The energy of edge-to-face interaction between two pyridine molecules, where both pyridines are with simultaneous hydrogen bonds; W1···P_d⊥P_a···W2 system was determined using the equation 6.

$$\Delta E\ (W1\cdots Pd \perp Pa\cdots W2) = E_{W1PdPaW2} - E_{W1Pd} - E_{PaW2} \qquad (6)$$

The change of strength of edge-to-face interactions between two pyridine molecules in W1···P_d⊥P_a···W2 and P_d⊥P_a systems, can be expressed by ΔΔE (the equation 7).

$$\Delta\Delta E = \Delta E\ (W1\cdots Pd \perp Pa\cdots W2) - \Delta E\ (Pd \perp Pa) \qquad (7)$$

S2. Model system for simultaneous CH/O interaction

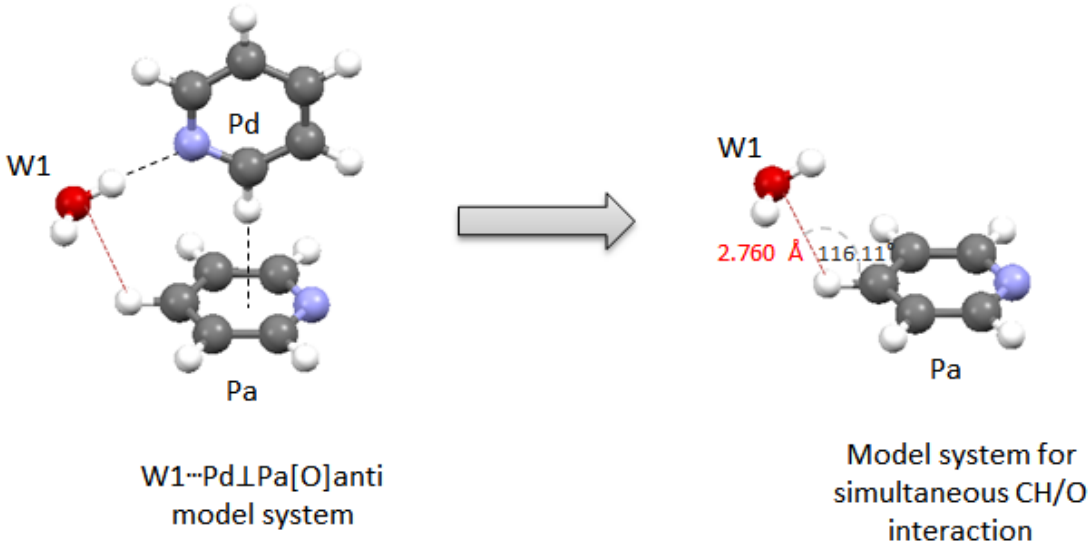

Figure S1. Model system used for calculations of simultaneous CH/O interaction.

S3. Optimization of water molecule in trimers

In both studied model systems, geometry of pyridine dimer was fixed while water molecule was optimized using MP2 method and cc-pVTZ basis set. In starting geometry, water molecule is perpendicular to the plane of pyridine and H···N distance is 2.0 Å in both model systems. In model system W1···P_d⊥ $P_{a[O]}$ *anti* system, H-O-H···N torsion angle is -119.43° while in model system P_d⊥P_a···W2 $_{[O]}$ *syn* the same angle is -0.10°. After optimization, the water molecule slightly changed its orientation. Namely, H···N distance in W1···P_d⊥ $P_{a[O]}$ *anti* system is 1.928 Å and H-O-

H···N torsion angle is 28.87°. H···N distance in W1···P_d⊥ $P_{a[O]}$ *anti* system is 1.956 Å and H-O-H···N torsion angle is -63.13°.

W1···P_d⊥ $P_{a[O]}$ *anti* P_d⊥P_a···$W2_{[O]}$ *syn*

Figure S2. Geometries of two systems with optimized water molecule.

S4. Cooperativity energies for model systems with hydrogen bonded pyridines

Since it was of interest to investigate the cooperative effects of three-body systems we performed calculations for all trimers to obtaine a quantitative account of cooperativity. Cooperativity energies, that consider interaction energies between all pairs of molecules, were calculated using the following expressions:

$$\Delta E_{Pyr1/Pyr2/W} = E_{Pyr1/Pyr2/W} - (E_{Pyr1}+E_{Pyr2}+E_w) \quad (8)$$

where $\Delta E_{Pyr1/Pyr2}$, $\Delta E_{Pyr1/W}$ and $\Delta E_{Pyr2/W}$ are pair interaction energies calculated using expressions:

$$\Delta E_{Pyr1/Pyr2} = E_{Pyr1/Pyr2} - (E_{Pyr1}+E_{Pyr2}) \quad (9)$$

$$\Delta E_{Pyr1/W} = E_{Pyr1/W} - (E_{Pyr1}+E_W)$$

$$\Delta E_{Pyr2/W} = E_{Pyr1/W} - (E_{Pyr2}+E_W)$$

$$\Delta E_{coop} = \Delta E_{Pyr1/Pyr2/W} - \Delta E_{Pyr/Pyr} - \Delta E_{Pyr1/W} - \Delta E_{Pyr2/W} \quad (10)$$

Cooperativity energy for four-body model system (tetramer) with the strongest edge-to-face interaction (-5.05 kcal/mol)

To investigate cooperative effects of four-body system we calculate cooperativity energy value (ΔE_{COOP}) for W1···P_d⊥P_a···W2 $_{[O]anti}$ tetramer using the following expression:

$$\Delta E_{coop} = E_{W1/Pyr1/Pyr2/W2} - (E_{W1} + E_{Pyr1} + \Delta E_{Pyr2} + E_{W2}) - (\Delta E_{W1/Pyr1} + \Delta E_{W1/Pyr2} + \Delta E_{W1/W2} + \Delta E_{Pyr1/Pyr2} + \Delta E_{Pyr1/W2} + \Delta E_{Pyr2/W2}) - (\Delta E_{W1/Pyr1/Pyr2} + \Delta E_{W1/Pyr1/W2} + \Delta E_{W1/Pyr2/W2} + \Delta E_{Pyr1/Pyr2/W2}) \quad (11)$$