Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Supplementary for:**

# Uracil-Water interaction revisited – In search of single H-bonded secondary minima

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**Table S1.** Hydrogen bond energies $E_{HB}$ (in kcal/mol) and relevant geometric parameters (length in Å) in trans- and cis-NMA complexes with a water molecule obtained by the M06-2X, MP2, B3LYP and B3LYP-D3, combined with aug-cc-pVTZ basis set.

| Complex | Vacuum | | | | Water | | | |
|---|---|---|---|---|---|---|---|---|
| | M06-2X | MP2 | B3LYP | B3LYP-D3 | M06-2X | MP2 | B3LYP | B3LYP-D3 |
| ***trans*-NMA-$H_2O$ (2A)** | | | | | | | | |
| $E_{int}$ | -8.56 | -8.37 | -6,71 | -8,59 | -5.95 | -6.03 | -4,52 | -6,18 |
| $C{=}O\cdots HO_w$ | 1.862 | 1.853 | 1.871 | 1.850 | 1.804 | 1.794 | 1.807 | 1.791 |
| ***trans*-NMA-$H_2O$ (2B)** | | | | | | | | |
| $E_{int}$ | -5.20 | -5.69 | -4,04 | -5,32 | -3,75 | -4,37 | -2.61 | -4.07 |
| $N\text{-}H\cdots O_w$ | 2.036 | 2.019 | 2.089 | 2.041 | 1,957 | 1,936 | 1.992 | 1.954 |
| ***cis*-NMA-$H_2O$ (2C)** | | | | | | | | |
| $E_{int}$ | -8.39 | -8.36 | -6,93 | -8.52 | -5.90 | -6.13 | -4,97 | -6,23 |
| $C{=}O\cdots HO_w$ | 1.842 | 1.832 | 1.848 | 1.839 | 1.774 | 1.767 | 1.779 | 1.767 |
| ***cis*-NMA-$H_2O$ (2D)** | | | | | | | | |
| $E_{int}$ | -10.75 | -10.73 | -9.00 | -10.72 | -6,35 | -6,53 | -4.94 | -6.64 |
| $C{=}O\cdots HO_w$ | 1,839 | 1,823 | 1.834 | 1.840 | 1,788 | 1,775 | 1.776 | 1.779 |
| $N\text{-}H\cdots O_w$ | 2,039 | 2,022 | 2.088 | 2.080 | 2,211 | 2,200 | 2.439 | 2.351 |

**Fig. S2** Optimized structures of *trans*-*N*-methylacetamide (**2A** and **2B**) complexes with a water molecule calculated with M06-2X, MP2, B3LYP, and B3LYP-D3, combined with aug-cc-pVTZ basis set in the gas-phase and water. Hydrogen bonds are marked with dotted lines, distances in Å, and angles in degrees.

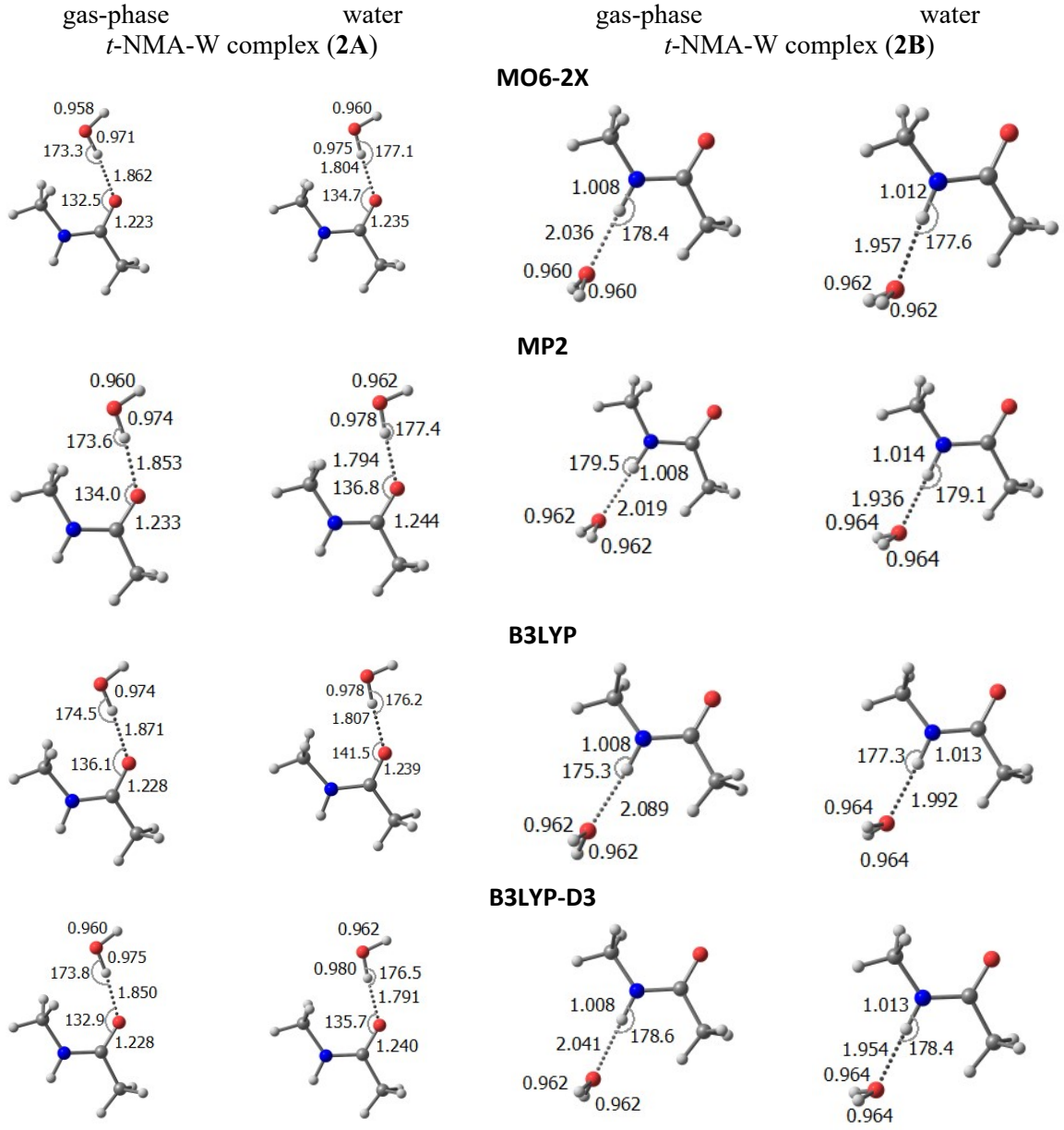


**Fig. S3** Optimized structures of *cis*-*N*-methylacetamide (**2C** and **2D**) complexes with a water molecule calculated with M06-2X, MP2, B3LYP, and B3LYP-D3, combined with aug-cc-pVTZ basis set in the gas-phase and water. Hydrogen bonds are marked with dotted lines, distances in Å, and angles in degrees.

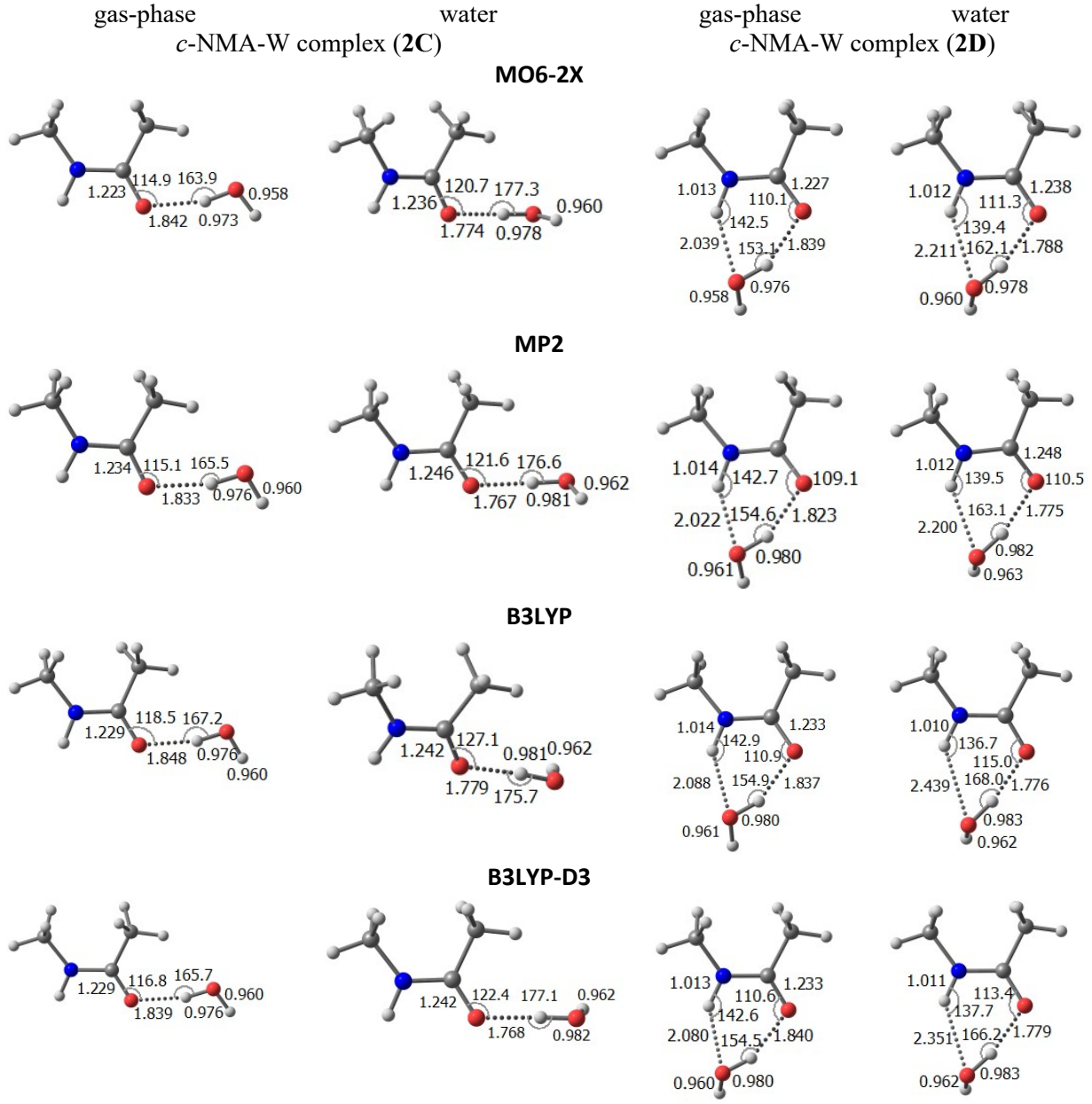


**Fig. S4** NPA charges (in e) of water, free and hydrated *trans*- (**2A** and **2B**) and *cis*- (**2C** and **2D,** Figure 2) NMA complexes with a water molecule obtained by the M06-2X/aug-cc-pVTZ method in the gas-phase and water.

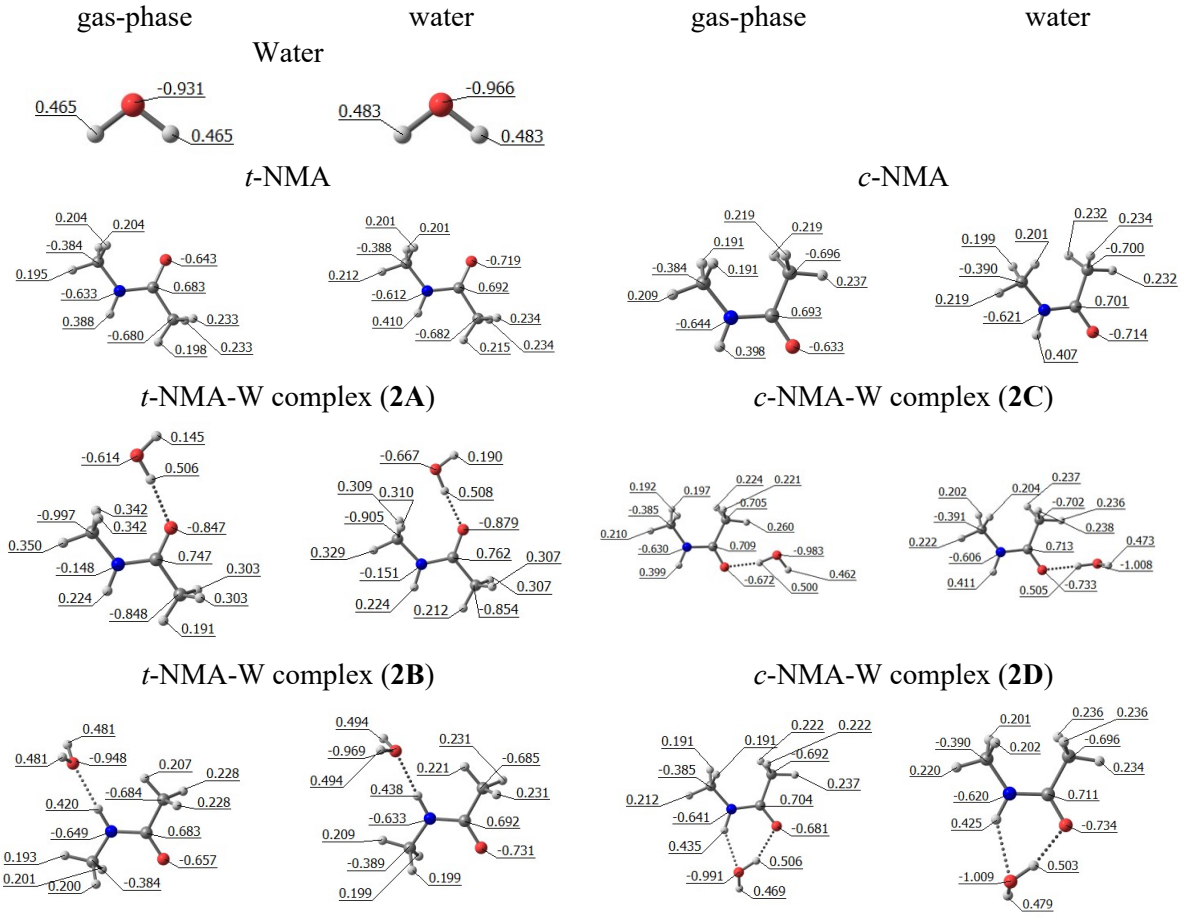


**Fig. S5** Optimized structures of uracil and water calculated with B3LYP, B3LYP-D3, M06-2X and MP2 combined with aug-cc-pVTZ basis set in the gas-phase and water., distances in Å,

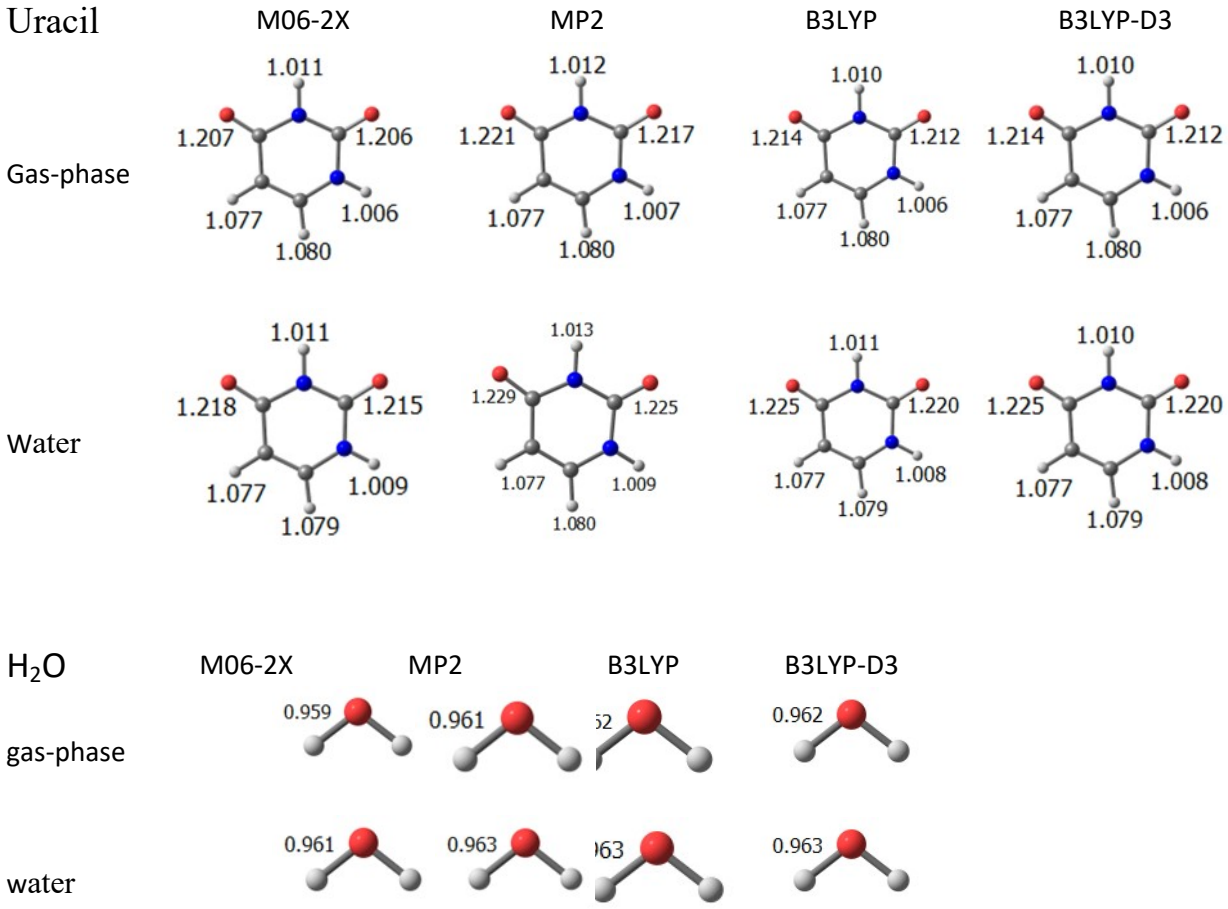
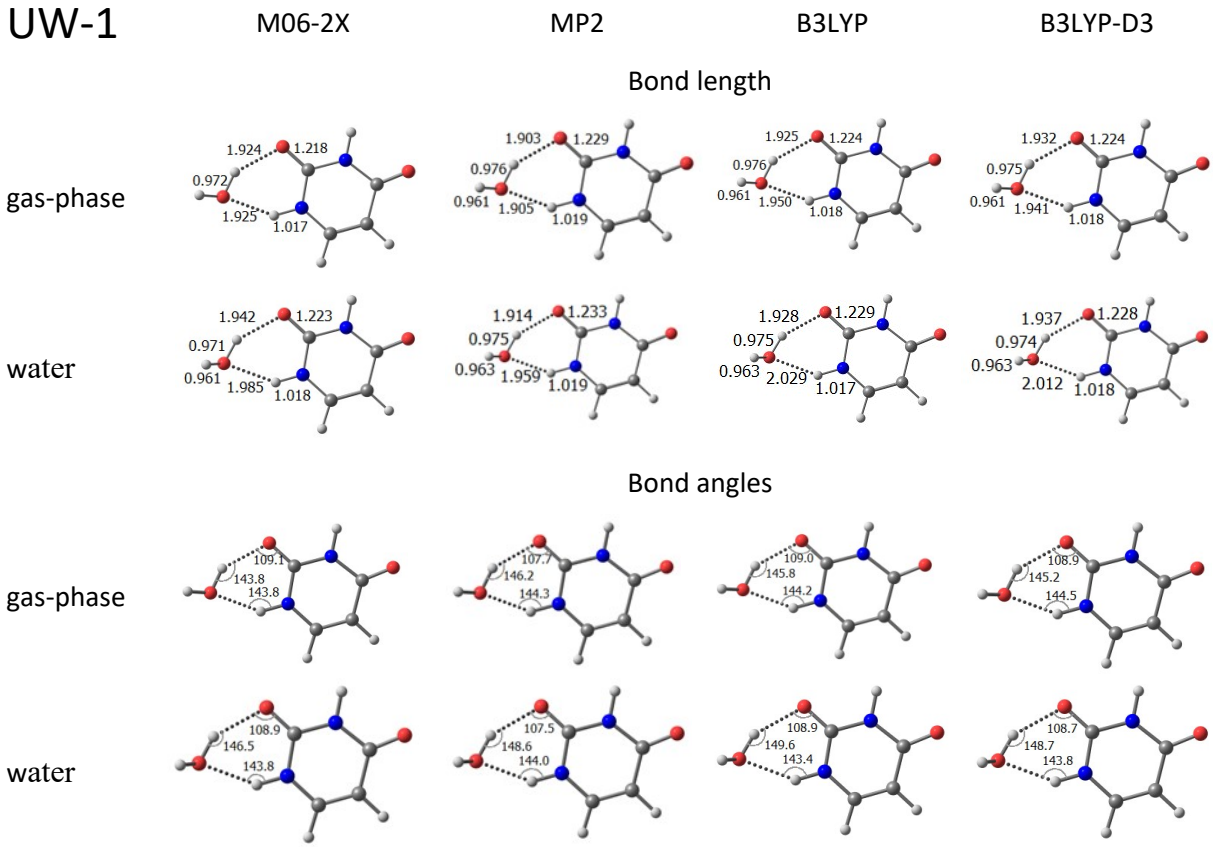
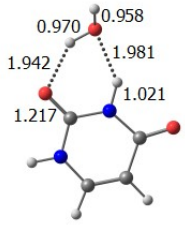
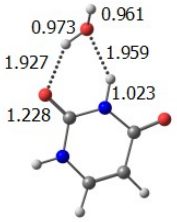
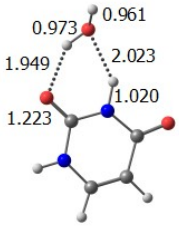
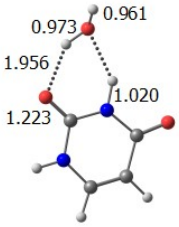
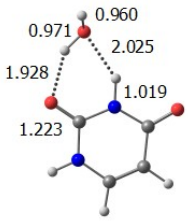
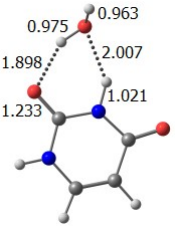
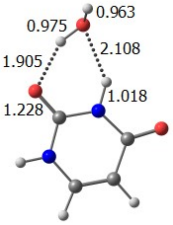
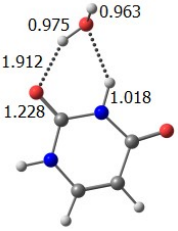
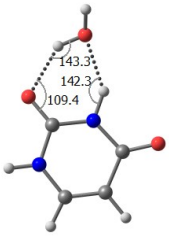
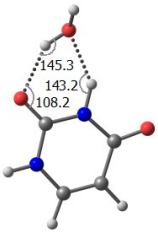
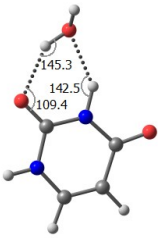
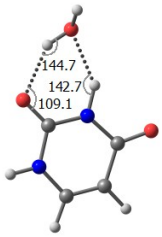
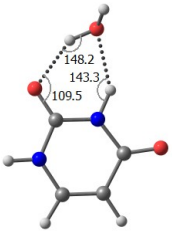
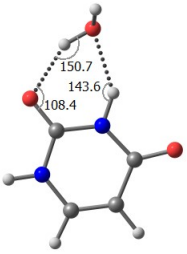
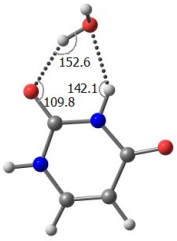
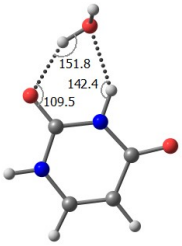


**Fig. S6** Optimized structures of double H-bonded uracil-water (UW-1, UW-2 and UW-3) calculated with M06-2X, MP2, B3LYP, and B3LYP-D3 combined with aug-cc-pVTZ basis set in the gas-phase and water. Distances are in Å and angles are in degrees.



UW-2

| | M06-2X | MP2 | B3LYP | B3LYP-D3 |
|---|---|---|---|---|
| **Bond length** | | | | |
| gas-phase |  |  |  |  |
| water |  |  |  |  |
| **Bond angles** | | | | |
| gas-phase |  |  |  |  |
| water |  |  |  |  |

UW-3

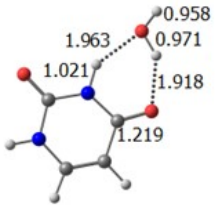
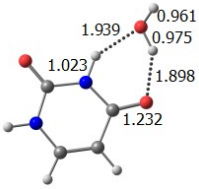
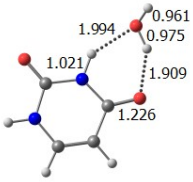
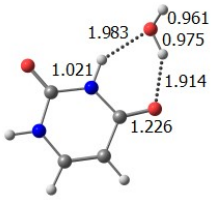
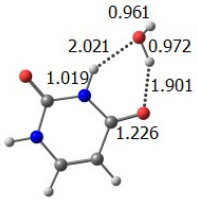
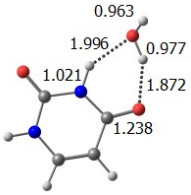
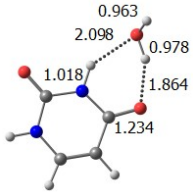
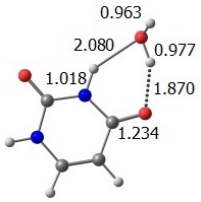
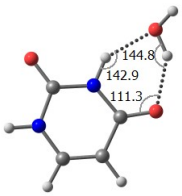
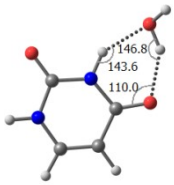
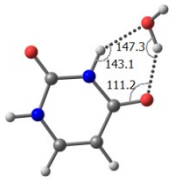
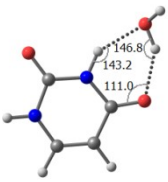
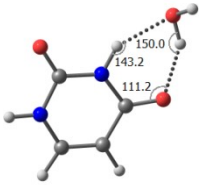
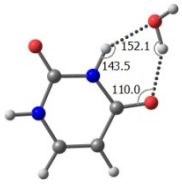
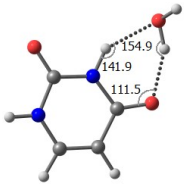
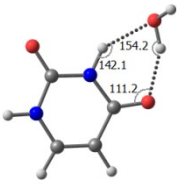
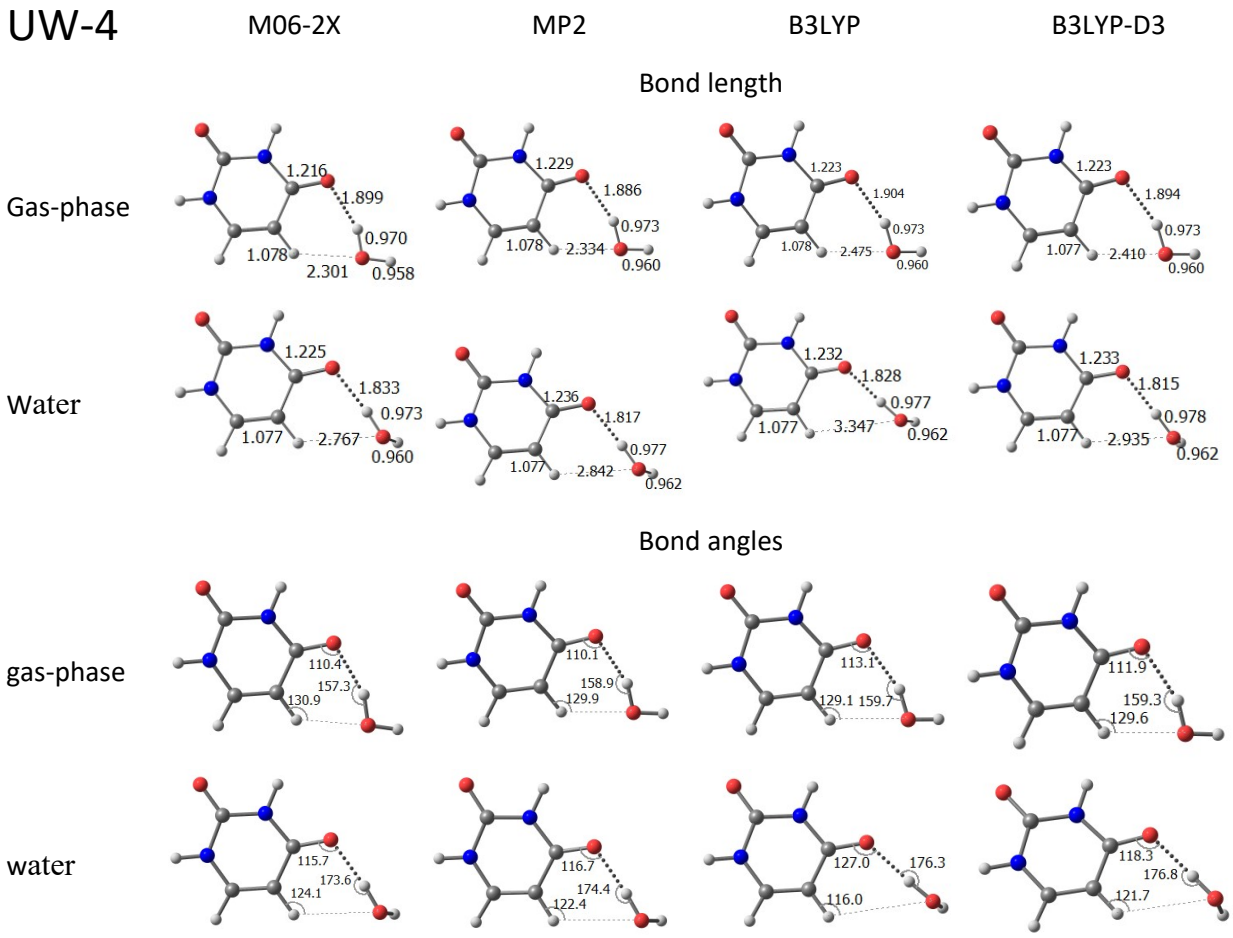
| | M06-2X | MP2 | B3LYP | B3LYP-D3 |
|---|---|---|---|---|
| **Bond length** | | | | |
| gas-phase |  |  |  |  |
| water |  |  |  |  |
| **Bond angles** | | | | |
| gas-phase |  |  |  |  |
| water |  |  |  |  |

**Fig. S7** Optimized structures of single H-bonded uracil-water (UW-4) calculated with M06-2X, MP2, B3LYP, and B3LYP-D3 combined with aug-cc-pVTZ basis set in the gas-phase and water. Distances are in Å and angles are in degrees.



**Tab. S8** The relative energies (in kcal/mol) of uracil-water complexes were calculated with M06-2X, MP2, B3LYP, and B3LYP-D3 combined with aug-cc-pVTZ basis set in vacuum and water.

| | Vacuum | | | | Water | | | |
|---|---|---|---|---|---|---|---|---|
| Complex | M06-2X | MP2 | B3LYP-D3 (B3LYP) | CCSD(T) | M06-2X | MP2 | B3LYP-D3 (B3LYP) | CCSD(T) |
| UW-1 | 0.00 | 0.00 | 0.00 (0.00) | 0.00 | 0.00 | 0.00 | 0.04 (0.04) | 0.00 |
| UW-2 | 2.05 | 1.98 | 2.04(2.07) | 1.88 | 0.31 | 0.29 | 0.36 (0.37) | 0.24 |
| UW-3 | 1.56 | 1.48 | 1.36 (1.38) | 1.48 | 0.10 | 0.07 | 0.00 (0.00) | 0.04 |
| UW-4 | 3.30 | 3.40 | 3.16 (3.10) | 3.42 | 1.27 | 1.17 | 0.84 (0.39) | 1.18 |
| UW-5 | 4.30 | 3.61 | 3.71 (3.12) | 3.62 | 1.34 | 0.83 | 0.93 (0.39) | 0.97 |
| UW-6 | NA | NA | NA | NA | 2.06 | 1.88 | 1.94 (0.92) | 2.10 |
| UW-7 | NA | NA | NA | NA | 1.80 | 1.43 | 1.60 (1.15) | 1.48 |

**Table S9** Number of Imaginary frequencies of UA-5 and UA-7 at fixed NH--O at 179.9° angles, where all other geometric parameters were relaxed during geometry optimization

| | M06-2X | | B3LYP | | B3LYP-D3 | |
|---|---|---|---|---|---|---|
| | Gas-phase | water | Gas-phase | water | Gas-phase | water |
| UW-5 | 1 (*65i*) | 0 | 1 (*49i*) | 0 | 1 (*59i*) | 0 |
| UW-7 | 1 (*81i*) | 0 | 1 (*60i*) | 0 | 1 (*71i*) | 0 |

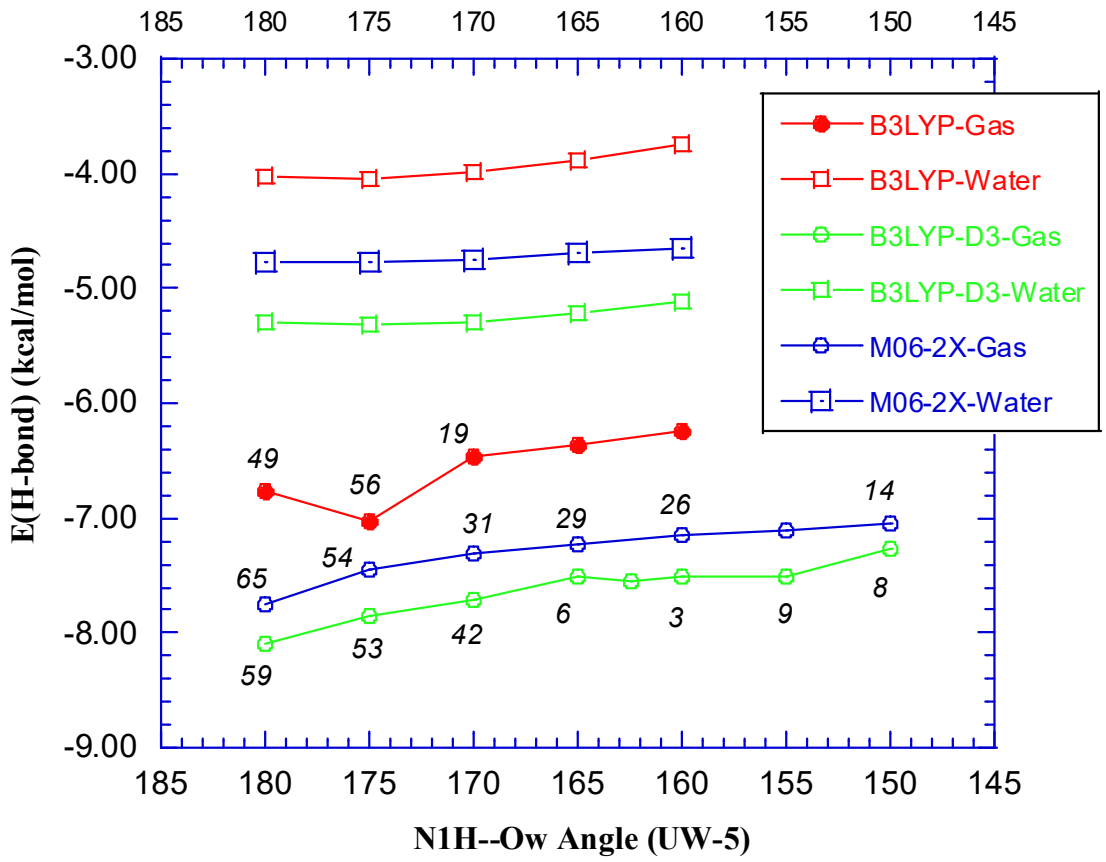



**Fig. S10** H-bond energy variation with N1H--$O_w$ angle of UW-5. The value of imaginary frequency (in $cm^{-1}$) is shown at each angle, points without a number indicate no imaginary mode. In water, all frequencies are real.

**Fig. S11** Optimized structures of single H-bonded uracil-water (UA-5, UA-6, and UA-7) calculated with M06-2X, MP2, B3LYP and B3LYP-D3 combined with aug-cc-pVTZ basis set in the gas-phase and water. Distances are in Å and angles are in degree.

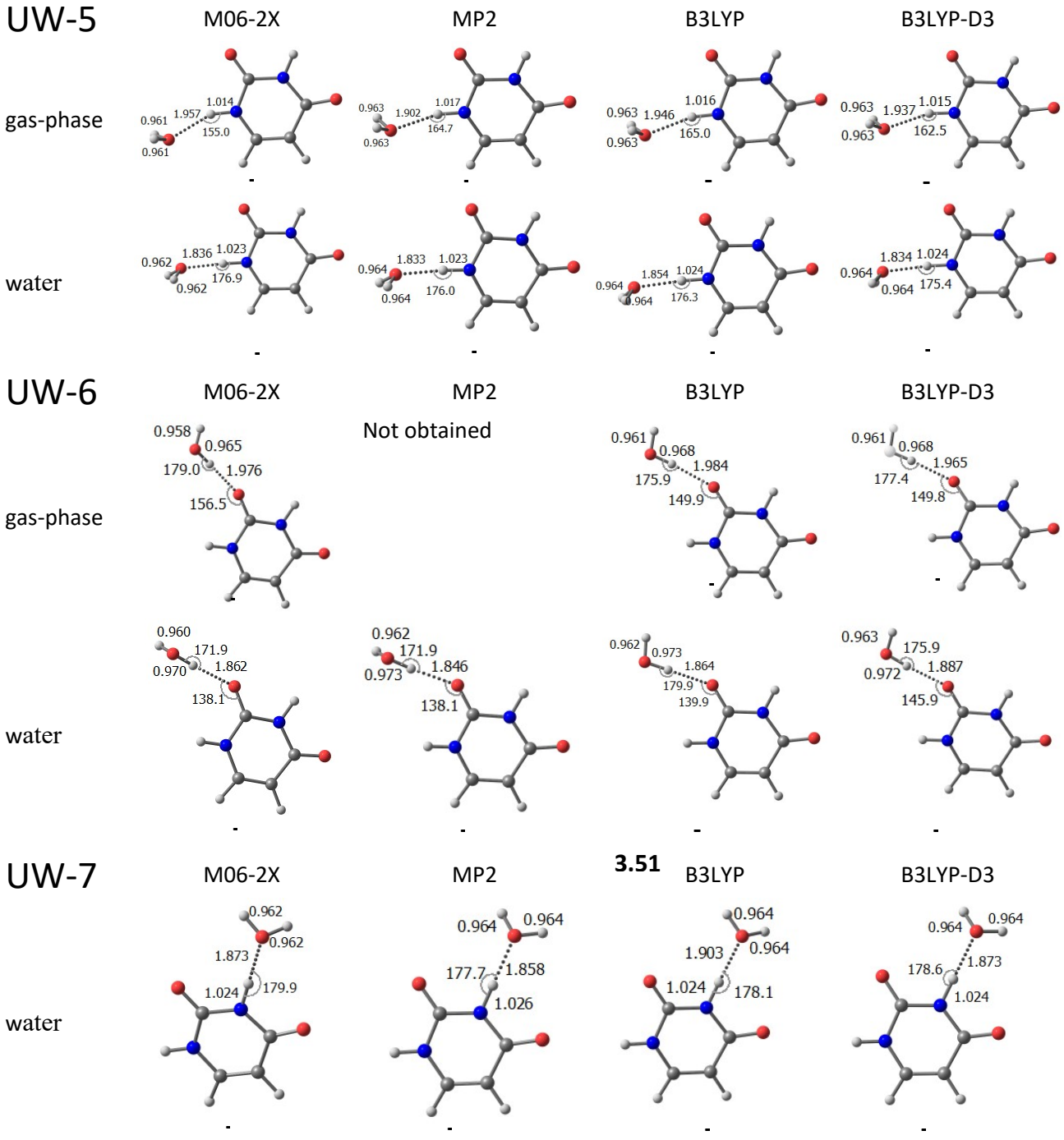
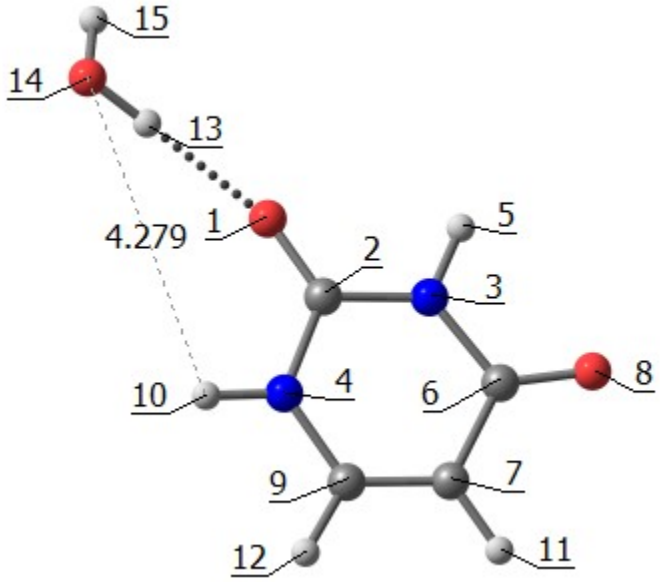


**Fig. S12** Numbering scheme of uracil-water UW-6 structure. Distance between O14 and H10 is shown in Å.




**Fixing and relaxing cartesian coordinate approach**:

In this approach, the selection of coordinates to be fixed in the first step should be limited to two atoms, such that those atoms are not directly connected, and also well-separated. The initial geometry of UW-6 was considered from the optimization using internal coordinates with two small imaginary frequencies and most likely close to the local minimum. The cartesian coordinates of atom Ow and the H atom of PD N1H (O14 and H10 in Fig. S12) were kept fixed during the first step of optimizations while all other atoms were allowed to move. The selection of these two atoms is because O14 is inclined towards the H10 and if allowed to move will form the UW-1 structure by further bending the C=O···H angle. The optimized structure thus obtained showed no imaginary frequency. In the next step, all optimized coordinates were held fixed and both O14 and H10 coordinates were optimized. Frequency calculation shows no imaginary vibrational mode in the second optimization step. Results thus obtained for UW-6 in the gas phase are given in Fig. S11, and H-bond energies are -5.15 kcal/mol (M06-2X), -4.88 (B3LYP) and -5.74 (B3LYP-D3). It may be noted that this approach did not work for UW-7 as more than a pair of atoms (both O of C=O and hydrogens of water) to be fixed, which will not allow the N2H···$O_w$ angle to change during optimization. However, such approach of obtaining local minimum requires further verification.

**Table S13**. Dipole moments (μ, in Debye) of monohydrated uracils and components and the effect of solvent (Δμ)

| Complex | Gas phase | Water | Δμ |
|---|---|---|---|
| U | 4.46 | 6.10 | 1.64 |
| W | 1.90 | 2.20 | 0.31 |
| UW-1 | 3.89 | 5.21 | 1.32 |
| UW-2 | 4.87 | 7.13 | 2.26 |
| UW-3 | 4.27 | 6.46 | 2.19 |
| UW-4 | 2.86 | 6.00 | 3.13 |
| UW-5 | 6.79 | 9.17 | 2.38 |
| UW-6 | | 5.90 | |
| UW-7 | | 4.27 | |