

Supplementary data for article:

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Supplementary Information for:

Nature of the water/aromatic parallel alignment interactions.

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The structure of the file:

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3. The ETS energy decomposition results based on BLYP-D3/TZ2P.
4. The orbital interaction based estimation of the leading bonding component $\Delta\rho_1$ ($\Delta E_{\text{orb}}(1)$) together with the charge estimations based on the NOCV eigenvalues.
5. Cartesian coordinates for the model systems.

1. Comparison of O-H bond lengths in bonded and non-bonded water molecules.

In order to examine $\pi \rightarrow \sigma^*(\text{O-H})$ charge transfer between benzene and water molecule a partial optimizations of all five model systems with MP2/cc-pVTZ method were done. During the optimizations the positions of all heavy atoms (carbons and oxygen) were constrained, and positions of hydrogen atoms were reoptimized. In all partially optimized structures elongation of the O-H bond(s) involved in interaction with benzene molecule were observed (Table S1). This elongation is largest in the B₂ model system (0.0031 Å), somewhat smaller for A₃ and B₁ model systems (0.0024 and 0.0021 Å) and smallest for A₁ and A₂ model systems (0.0013 Å). The calculated variation in OH bond lengths by 0.0013-0.0031 Å is rather subtle, concerning the accuracy of the calculations. However, the largest OH bond elongation observed for B₂ is fully consistent with the results of the NOCV analysis, indicating the largest $\Delta E_{\text{orb}}(1)$ energy contribution for this structure.

Table S1. O-H bond lengths of the interacting hydrogen atom(s) in partially optimized model systems.	
Structure	O-H bond length (Å) for interacting hydrogen atom*
B ₂	0.9621
B ₁	0.9611
A ₃	0.9614
A ₂	0.9603, 0.9603
A ₁	0.9603, 0.9603

*O-H bond length in non-bonded water molecule, optimized with MP2/cc-pVTZ method is 0.9590 Å

2. Construction of the model systems.

Model systems for the interaction energy calculations were constructed based on extensive analysis of the data about water/aromatic parallel alignment in crystal structures from CSD. Analysis of the data obtained from CDS search on the angle between planes of water molecule and aromatic group have shown that majority of the structures can be divided in to two sets: (i) the angle between planes are 0° i.e. the water molecule and aromatic group lies in parallel planes (set A); (ii) only one O-H bond from water molecule is parallel to the aromatic ring plane (set B).^[30-32] Further analysis of the data obtained from CSD have shown that, for the structures belonging to A set, there are three most common orientations of water molecule with respect to aromatic group: (i) symmetric orientation (C_s symmetry point group) with water molecule σ_v reflection plane overlapping with aromatic group σ_v reflection plane (the reflection plane that goes through opposite carbon atoms) – model system A_1 ; (ii) symmetric orientation (C_s symmetry point group) with water molecule σ_v reflection plane overlapping with aromatic group σ_d reflection plane (the reflection plane that bisects opposite C–C bonds) – model system A_2 ; (iii) asymmetric orientation – model system A_3 . All the structures from B set are represented with two model systems: model system B_1 - water molecule σ_v' reflection plane overlapping with aromatic group σ_v reflection plane and model system B_2 - water molecule σ_v' reflection plane overlapping with aromatic group σ_d reflection plane. Both model systems for B set are symmetric (C_s point group). Model systems A_0 and B_0 have the same symmetry as A_2 and B_1 model systems.

In order to find the optimal geometry of the complex for every model system a number of single point supramolecular interaction energy calculations were done (with MP2/cc-pVTZ level of theory) by varying the horizontal displacement value in range from 1.5 - 3.5 Å (0.0 - 1.5 Å for A_0 and B_0 model systems) and for every horizontal displacement value varying the normal distance until the structure with the lowest energy was found. Structures with the lowest energy for every model system are shown on Figure 1, and the corresponding horizontal displacement values and normal distances are shown in Table 1. No further geometry optimization was employed.

At this point, it is important to notice that these geometries are not the global minima for water/benzene system. The full optimization (without BSSE correction) of every model system leads to the global minimum for water-benzene system, with OH/ π interaction between molecules (Figure S1).

The geometries of isolated molecules, benzene and water molecule were optimized at MP2/cc-pVTZ level.

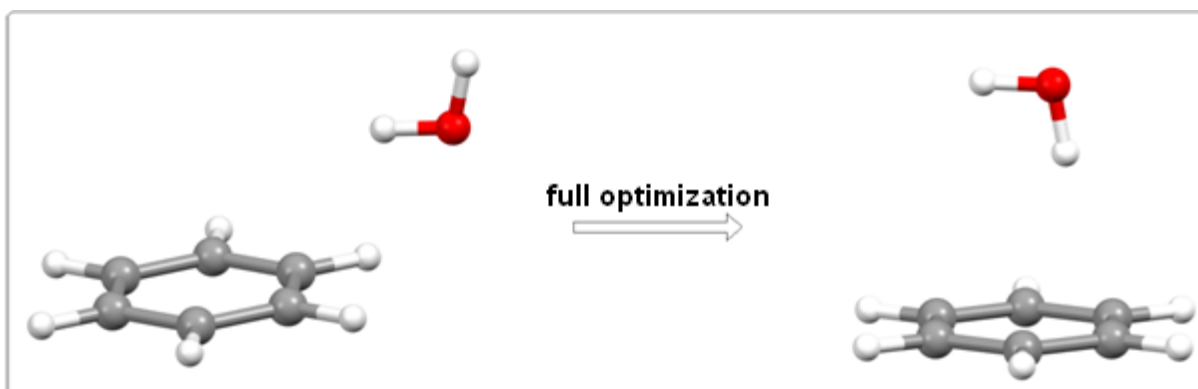


Figure S1. The full optimization of most stable parallel water/benzene dimer geometry (B₂ model system) leads to the geometry with OH/ π interaction.

3. The ETS energy decomposition results based on BLYP-D3/TZ2P.

Table S2. ETS energy decomposition based on BLYP-D3.

Model System	A ₁	A ₂	A ₃	B ₁	B ₂	A ₀	B ₀
<i>BLYP-D3</i>							
$\Delta E_{\text{total}}^*$	-1.55	-1.67	-1.93	-2.29	-2.64	-0.64	-0.62
ΔE_{orb}	-0.45	-0.67	-0.61	-0.86	-1.01	-0.40	-0.28
ΔE_{elstat}	-1.25	-2.01	-1.31	-2.05	-2.15	-0.23	-0.19
ΔE_{Pauli}	1.60	3.20	1.57	2.39	2.53	1.47	1.32
ΔE_{disp}	-1.45	-2.18	-1.58	-1.77	-2.01	-1.47	-1.47

$$\Delta E_{\text{total}} = \Delta E_{\text{orb}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{disp}}$$

It is clear from the Table S2 that the total interaction energy for the B set model systems are notably more negative than for the A set model systems. The weakest interactions are for A₀ and B₀ model systems. These results are fully in line with both the PBE-D3 results as well as the SAPT data. One should add that the trend in the orbital interaction energy is preserved when comparing PBE-D3 and BLYP-D3.

4. The orbital interaction based estimation of the leading bonding component $\Delta\rho_1$ ($\Delta E_{\text{orb}}(1)$) together with the charge estimations based on the NOCV eigenvalues.

Table S3. The orbital interaction based estimation of the leading bonding component ($\Delta E_{\text{orb}}(1)$) together with the charge estimations based on NOCV eigenvalues.

	A ₁	A ₂	A ₃	B ₁	B ₂	A ₀	B ₀
$\Delta E_{\text{orb}}(1)$ (kcal/mol)	-0.1962	-0.2665	-0.2690	-0.4098	-0.5260	-0.1443	-0.1145
$ v_1 $ (a.u.)	0.0401	0.0483	0.0461	0.0539	0.0610	0.0277	0.0263

5. Cartesian coordinates for the model systems.

Cartesian coordinates for A₁ model system

C -0.557692 0.771738 0.000000
C -0.557692 0.074938 1.206893
C -0.557692 -1.318662 1.206893
C -0.557692 -2.015462 0.000000
C -0.557692 -1.318662 -1.206893
C -0.557692 0.074938 -1.206893
H -0.557692 1.853038 0.000000
H -0.557692 0.615588 2.143326
H -0.557692 -1.859312 2.143326
H -0.557692 -3.096762 0.000000
H -0.557692 -1.859312 -2.143326
H -0.557692 0.615588 -2.143326
O 2.342308 2.721838 0.000000
H 2.265958 2.281821 -0.848668
H 2.342275 2.168331 0.783142

Cartesian coordinates for A₂ model system

C -0.538462 0.670355 0.696800
C -0.538462 -0.536538 1.393600
C -0.538462 -1.743431 0.696800
C -0.538462 -1.743431 -0.696800
C -0.538462 -0.536538 -1.393600
C -0.538462 0.670355 -0.696800
H -0.538462 1.606789 1.237450
H -0.538462 -0.536538 2.474900
H -0.538462 -2.679864 1.237450
H -0.538462 -2.679864 -1.237450
H -0.538462 -0.536538 -2.474900
H -0.538462 1.606789 -1.237450

O	2.261538	2.363462	0.000000
H	2.261486	1.810010	0.783181
H	2.261493	1.809969	-0.783152

Cartesian coordinates for A₃ model system

C	-0.248784	0.669132	0.656216
C	0.816052	1.395339	0.126244
C	1.914154	0.728377	-0.413622
C	1.947421	-0.664790	-0.423516
C	0.882585	-1.390997	0.106455
C	-0.215517	-0.724036	0.646321
H	-1.100806	1.186630	1.075100
H	0.790241	2.476303	0.133922
H	2.740365	1.291844	-0.824829
H	2.799442	-1.182288	-0.842401
H	0.908396	-2.471961	0.098778
H	-1.041728	-1.287502	1.057528
O	-3.621889	-0.100491	-0.461165
H	-2.762581	-0.076910	-0.886271
H	-3.930232	0.795402	-0.312905

Cartesian coordinates for B₁ model system

C	-0.498702	0.742521	0.000000
C	-0.498702	0.045721	1.206893
C	-0.498702	-1.347879	1.206893
C	-0.498702	-2.044679	0.000000
C	-0.498702	-1.347879	-1.206893
C	-0.498702	0.045721	-1.206893
H	-0.498702	1.824021	0.000000
H	-0.498702	0.586471	2.143499
H	-0.498702	-1.888629	2.143499
H	-0.498702	-3.126179	0.000000
H	-0.498702	-1.888629	-2.143499
H	-0.498702	0.586471	-2.143499
O	2.001298	2.808021	0.000000
H	2.001298	1.848921	0.000000
H	2.933819	3.032244	0.000000

Cartesian coordinates for B₂ model system

C	-0.460129	0.540593	0.698500
C	-0.460129	-0.669245	1.397000
C	-0.460129	-1.879082	0.698500
C	-0.460129	-1.879082	-0.698500
C	-0.460129	-0.669245	-1.397000
C	-0.460129	0.540593	-0.698500
H	-0.460129	1.477026	1.239150
H	-0.460129	-0.669245	2.478300
H	-0.460129	-2.815515	1.239150
H	-0.460129	-2.815515	-1.239150

H	-0.460129	-0.669245	-2.478300
H	-0.460129	1.477026	-1.239150
O	1.839871	2.883855	0.000000
H	1.839872	1.924855	-0.000012
H	2.772306	3.108013	0.000034

The coordinates of optimized geometry

C	-1.054161	0.724202	0.697411
C	-0.469564	-0.332599	1.394557
C	0.113952	-1.389113	0.697176
C	0.113952	-1.389113	-0.697176
C	-0.469564	-0.332599	-1.394557
C	-1.054161	0.724202	-0.697411
H	-1.504973	1.544971	1.237994
H	-0.466899	-0.330621	2.475753
H	0.565889	-2.209284	1.238057
H	0.565889	-2.209284	-1.238057
H	-0.466899	-0.330621	-2.475753
H	-1.504973	1.544971	-1.237994
O	2.322398	1.666882	0.000000
H	1.410881	1.359452	0.000000
H	2.822987	0.848904	0.000000

Cartesian coordinates for A₀ model system

C	-0.378600	-0.697160	1.254460
C	-0.378450	0.696440	1.254860
C	-0.692780	1.393610	0.089840
C	-1.007270	0.697180	-1.075580
C	-1.007420	-0.696420	-1.075970
C	-0.693080	-1.393590	0.089040
H	-0.134700	-1.238090	2.158410
H	-0.134430	1.236810	2.159110
H	-0.692670	2.474910	0.090150
H	-1.251170	1.238110	-1.979520
H	-1.251430	-1.236790	-1.980230
H	-0.693200	-2.474890	0.088740
O	2.938980	-0.000080	-0.269460
H	2.794793	-0.783100	-0.804036
H	2.794956	0.783278	-0.803584

Cartesian coordinates for B₀ model system

C	-0.557692	0.771738	0.000000
C	-0.557692	0.074938	1.206893
C	-0.557692	-1.318662	1.206893
C	-0.557692	-2.015462	0.000000
C	-0.557692	-1.318662	-1.206893

C	-0.557692	0.074938	-1.206893
H	-0.557692	1.853038	0.000000
H	-0.557692	0.615588	2.143326
H	-0.557692	-1.859312	2.143326
H	-0.557692	-3.096762	0.000000
H	-0.557692	-1.859312	-2.143326
H	-0.557692	0.615588	-2.143326
O	-3.957692	0.771738	0.000000
H	-3.957692	-0.187262	0.000000
H	-4.861685	1.091859	0.000000