CHEMPHYSCHEM

Supporting Information

Interactions of Aromatic Radicals with Water

Rachel Crespo-Otero,[a] Kenny Bravo-Rodriguez,[a] Saonli Roy,[b] Tobias Benighaus,[a] Walter Thiel,[a] Wolfram Sander,[b] and Elsa Sánchez-García*[a]

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Supplementary Information

Figure 1S. Radical ••• water complexes which are transition states (TS) with B3LYP-D. The M05-2X (a) and B3LYP-D (b) interacting distances are shown in Angstroms (Å).

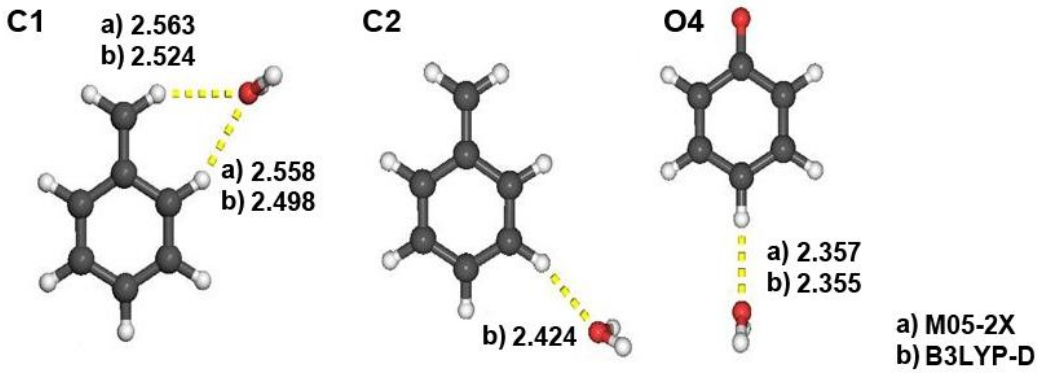
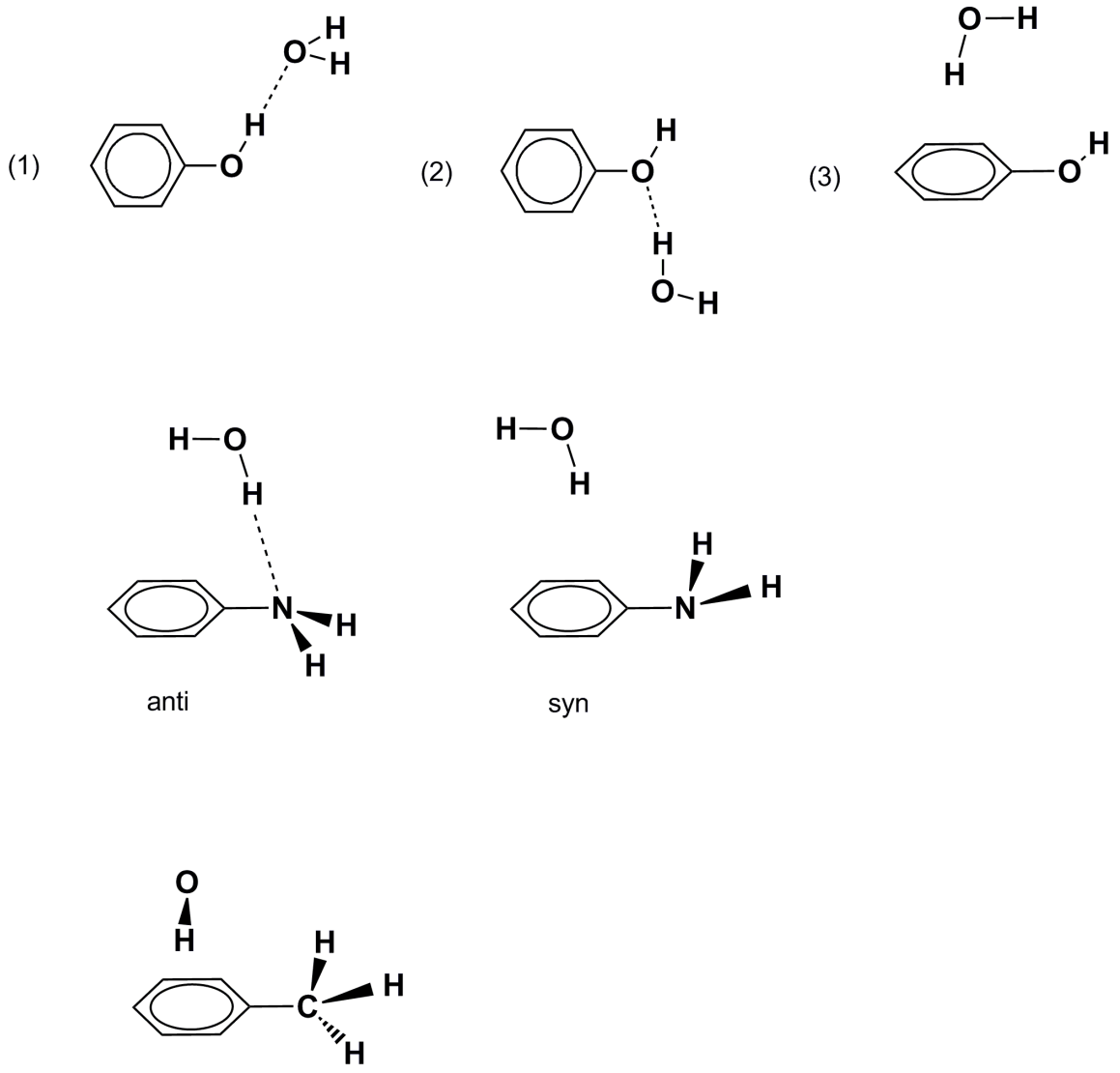


Figure 2S. Phenol, aniline and toluene complexes with water (1-3).



1. Bandyopadhyay, I., H.M. Lee, and K.S. Kim, *Phenol vs Water Molecule Interacting with Various Molecules: σ-type, π-type, and χ-type Hydrogen Bonds, Interaction Energies, and Their Energy Components.* The Journal of Physical Chemistry A, 2005. **109**(8): p. 1720-1728.
2. Piani, G., et al., *The aniline–water and aniline–methanol complexes in the S1 excited state.* Chemical Physics, 2006. **330**(1–2): p. 138-145.
3. Tarakeshwar, P., K.S. Kim, and B. Brutschy, *Interaction of the water dimer with pi-systems: A theoretical investigation of structures, energies, and vibrational frequencies.* The Journal of Chemical Physics, 2000. **112**(4): p. 1769-1781.

Figure 3S. Snapshots of complex **C1** (which converts to **C6** at 100K) from the UB3LYP-D/6-311++G(2d,2p) MD simulations at T=100K (top) and T=298K (bottom). Time is shown in picoseconds (ps).

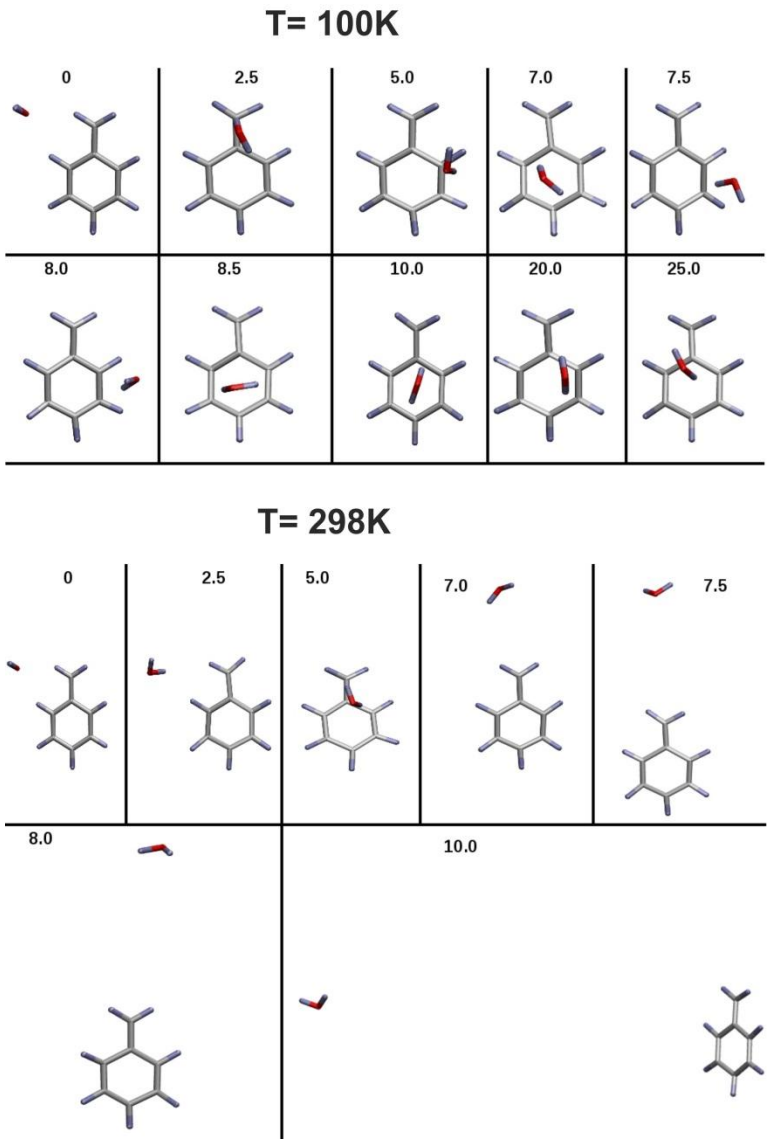


Figure 4S. Snapshots of complex **N1** from the UB3LYP-D/6-311++G(2d,2p) MD simulations at T=100K (top) and T=298K (bottom). Time is shown in picoseconds (ps).

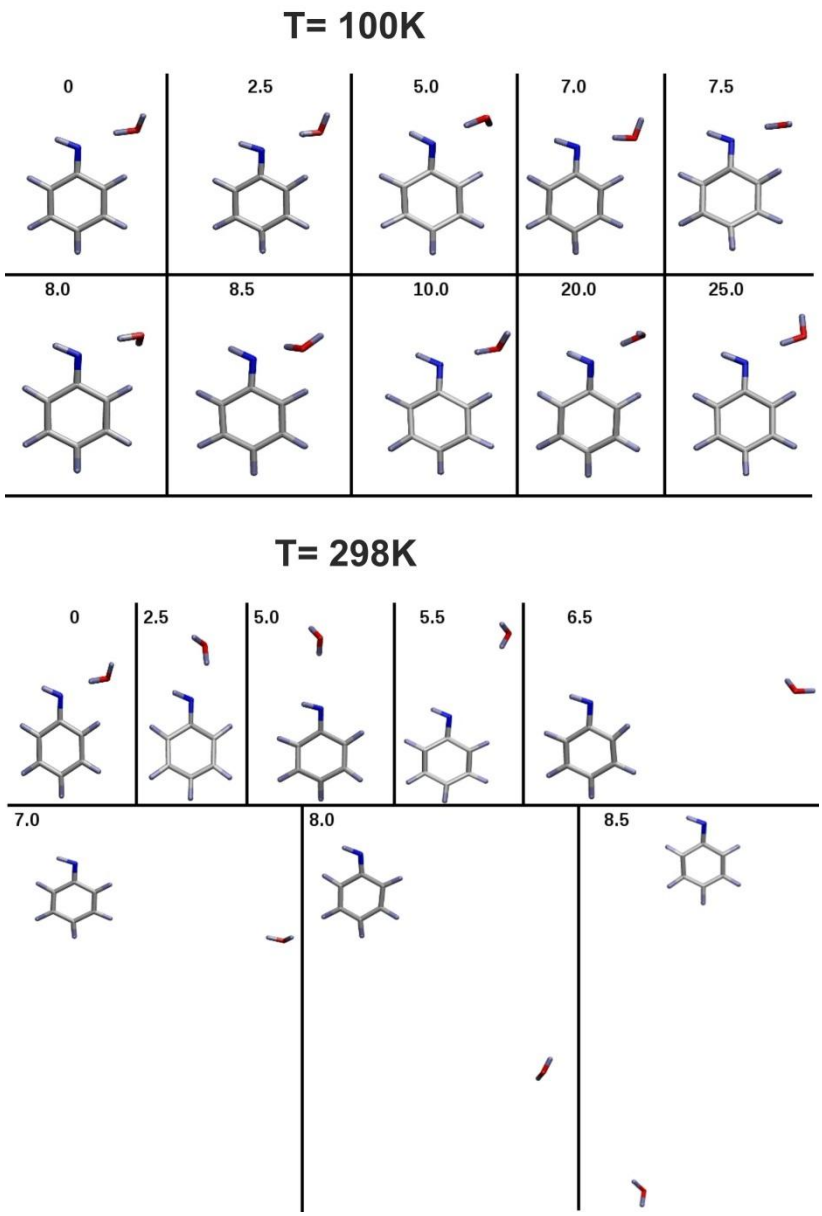


Figure 5S. Snapshots of complex **O1** from the UB3LYP-D/6-311++G(2d,2p) MD simulations at T=100K (top) and T=298K (bottom). Time is shown in picoseconds (ps).

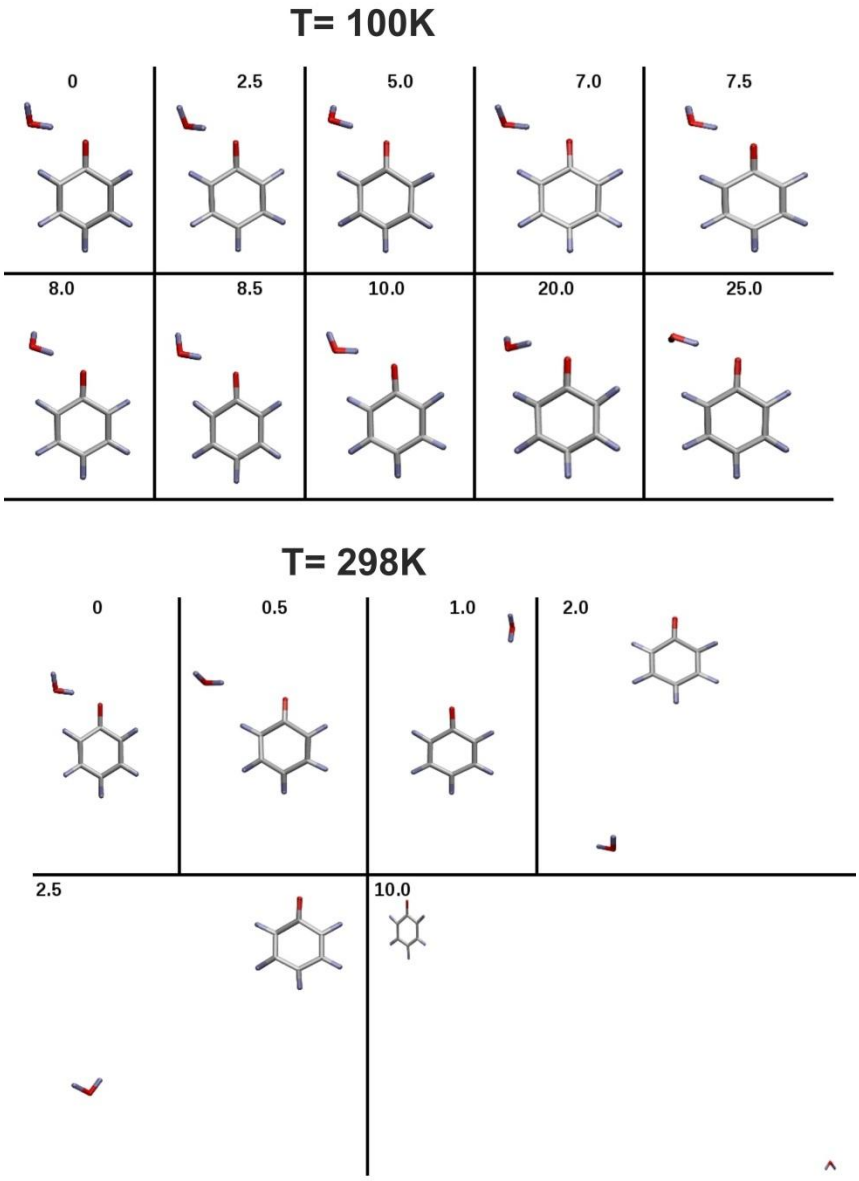


Table 1S. Interaction energies (ΔE) for the radical ••• water complexes which are transition states (TS) with B3LYP-D. Basis set superposition error corrected energies (ΔE_{BSSE}) are also included. All energies are in kcal/mol.

	6-311++G(2d,2p)				
Transition States	B3LYP		M05-2X		B3LYP-D
B3LYP-D	ΔE	ΔE_{BSSE}	ΔE	ΔE_{BSSE}	ΔE
C complex					
C1	-1.23	-0.23	-2.29	-1.12	-2.37
C2	-1.01	-0.24		**C6**	-1.71
O complex					
O4	-1.93	-1.09	-2.58	-1.49	-2.66

Table 2S. Comparison between the calculated spectra of complexes C6 and C7. Values for frequencies (v) are in cm^{-1} while intensities (I) are in $km \cdot mol^{-1}$.

C6				C7			
B3LYP		M05-2X		B3LYP		M05-2X	
v	I	v	I	v	I	v	I
45.23	1.0	34.43	1.8	51.88	3.9	41.07	0.2
54.17	0.5	47.61	0.6	62.36	21.6	57.31	3.3
115.58	0.8	97.96	2.6	79.21	3.6	103.49	6.4
131.52	1.5	128.8	5.3	112.03	52.2	116.23	21.9
198.71	21.2	202.52	17.9	136.24	0.5	200.15	53.5
209.19	49.2	222.39	57.2	198.27	2.3	208.10	23.8
255.76	105.5	257.83	122.2	290.89	91.7	298.67	91.7
361.16	0.2	358.05	0.4	359.60	0.1	359.69	0.3
392.32	0.3	394.86	0.1	390.58	0.0	397.27	0.0
478.40	16.6	482.96	18.6	473.68	13.6	483.98	15.4
518.75	0.0	509.16	0.0	514.90	0.0	507.44	0.0
534.17	0.2	535.78	0.2	533.84	0.1	536.16	0.2
627.74	0.1	630.75	0.0	628.14	0.0	631.38	0.0
681.31	46.3	**697.25**	48.4	672.42	42.1	**700.19**	47.4
726.44	0.6	745.47	0.1	727.16	0.4	751.65	0.1
780.82	68.2	**801.25**	80.1	777.65	71.6	**804.64**	79
829.17	0.3	845.45	0.4	829.33	0.3	846.88	0.4
836.02	0.0	855.11	0.0	840.37	0.0	865.30	0.0
906.46	3.9	**931.42**	4.2	905.05	7.2	**935.07**	6.5
977.52	2.0	986.91	1.5	975.86	1.9	990.13	1.5

983.38	0.0	1006.92	0.0	986.63	0.0	1009.60	1.2
992.76	0.1	1009.21	1.1	991.48	0.3	1013.94	0.0
995.55	1.3	1019.12	0.0	994.85	1.2	1023.41	0.0
1030.57	1.7	1056.11	2.3	1030.87	2.0	1057.61	2.4
1116.27	2.4	1133.78	3.6	1115.08	2.2	1134.52	3.3
1174.20	0.0	1182.18	0.0	1174.25	0.2	1183.89	0.1
1184.99	0.3	1195.18	0.4	1183.10	0.3	1196.76	0.4
1287.25	1.3	1300.21	1.1	1288.94	1.3	1304.18	1.0
1318.85	0.4	1336.09	0.2	1319.22	1.8	1339.16	0.9
1357.68	0.8	1374.39	0.6	1357.31	0.4	1376.35	0.4
1474.83	6.4	1507.39	8.0	1474.71	5.1	1508.95	7.3
1496.35	0.1	1516.23	1.0	1495.58	0.0	1519.72	0.7
1504.16	12.4	1529.65	16.0	1504.66	12.4	1533.57	16.9
1569.08	1.2	1621.41	1.0	1569.90	1.4	1623.35	1.4
1589.79	0.5	1637.99	31.2	1586.55	0.9	1638.56	7.1
1659.43	139.6	1642.32	109.5	1664.19	172.1	1644.38	127.6
3142.12	3.8	3233.32	1.8	3142.93	3.6	3231.32	1.7
3166.07	4.3	3249.57	3.9	3163.64	5.7	3244.80	3.4
3168.59	0.5	3251.18	0.8	3166.02	0.3	3250.52	1.4
3179.28	3.6	3262.58	1.1	3178.43	2.2	3259.27	3.4
3184.57	21.4	3267.55	12.7	3181.47	22.4	3264.94	11.3
3195.89	7.2	3279.85	4.6	3196.33	7.5	3277.43	4.4
3240.77	5.3	3334.51	2.2	3241.37	5.5	3331.82	2.4
3804.67	49.3	3864.51	62.1	3807.62	42.8	3857.56	79.6
3890.79	22.5	3957.49	39.1	3882.81	20.5	3960.35	54.3