TABLE S 7: Comparison of the Results of Re-optimization in Solution of Conformers without the Intramolecular H-bond, when Using the Corresponding In-vacuo Optimized Conformer as Input, and when Removing the H-bond from the Conformer Optimised in Solution.
The values *in vacuo* are reported to facilitate the comparison between the evaluation of the energy increase on H-bond removal when O11 rotates off-plane and when it does not. For the cases *in vacuo* with R≠H, O11 always rotates off-plane on optimization, and the values for a planar orientation were obtained by freezing O11 at the angle it has when engaged in the H-bond [19].

a) Comparison of relative energies.
For each structure, the relative energies are referred to the lowest energy conformer of that structure.
The values written in red correspond to the cases in which O11 does not rotate off-plane.

	Relative energy (kcal/mol)							
Structure and conformer	*in vacuo*		in chloroform		in acetonitrile		in water	
	input with O11 free to rotate	input with O11 frozen on the plane	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input
A-w [a]	14.887	–	10.625	–	9.570	–	7.579	–
A-r [a]	15.792	–	12.963	–	12.307	–	10.520	–
AA-w [a]	13.305	–	9.837	–	8.123	–	5.078	–
B-w	12.978	16.118	10.229	13.225	9.375	12.350	7.293	7.927
B-r	14.694	18.011	12.274	12.849	11.799	11.651	9.929	10.057
BB-w	13.140	15.725	9.968	12.462	8.573	8.903	5.544	5.743
D-w	12.000	16.047	9.275	13.319	8.394	12.474	6.334	6.334
D-r	13.841	17.936	11.351	11.351	10.760	–	8.616	8.615
DD-w	12.230	15.693	6.676	9.065	7.612	7.619	4.652	4.652
E1-w	11.928	16.052	9.198	9.243	8.352	8.344	6.220	6.220
E1-r	13.464	17.939	11.196	11.259	10.710	10.564	8.643	8.493
EE1-w	12.231	15.698	6.604	11.800	3.896	5.498	4.524	4.526
E2-w	10.762	15.147	8.058	8.129	7.177	7.293	5.066	5.174
E2-r	12.506	16.764	10.178	10.158	9.666	9.470	7.631	7.335
EE2-w	10.974	16.090	5.409	7.909	6.407	6.407	3.334	3.334
F1-w	11.914	16.062	9.175	13.330	8.321	8.302	6.232	6.232
F1-r	13.449	17.951	11.165	11.229	10.653	10.582	8.635	8.485
FF1-w	12.150	15.710	8.951	8.983	7.526	11.175	4.501	4.495
L-w	11.640	15.264	8.731	8.803	7.677	7.782	5.379	5.562
L-r	13.493	16.411	10.210	10.843	10.912	10.173	8.078	8.039
LL-w	11.741	15.010	8.520	8.520	6.798	6.809	3.534	3.541

b) Comparison of energy increase on H-bond removal.
The values written in red correspond to the cases in which O11 does not rotate off-plane.

	Energy increase on H-bond removal (kcal/mol)							
Structure and conformer	*in vacuo*		in chloroform		in acetonitrile		in water	
	input with O11 free to rotate	input with O11 frozen on the plane	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input
A-d-w [a]	13.870	–	10.625	–	9.570	–	7.579	–
A-s-r [a]	12.105	–	9.285	–	7.972	–	5.088	–
AA-d-w [a]	11.914	–	9.158	–	7.808	–	4.916	–
B-d-w	12.098	15.574	10.229	13.225	9.375	12.350	7.293	7.927
B-s-r	10.837	14.154	8.322	8.898	7.403	7.254	4.200	4.327
BB-d-w	11.621	14.207	9.216	11.710	8.217	8.548	5.377	5.576
D-d-w	11.148	15.195	9.275	13.319	8.394	12.474	6.334	6.334
D-s-r	9.677	14.077	7.484	7.484	6.433	–	3.031	3.031
DD-d-w	10.712	14.175	8.279	8.314	7.254	7.619	4.448	4.652
E1-d-w	11.079	15.203	9.198	9.243	8.352	8.344	6.220	6.220
E1-s-r	9.606	14.082	7.339	7.403	6.353	6.207	3.022	2.872
EE1-d-w	10.715	14.183	5.832	11.048	7.241	7.240	4.341	4.526
E2-d-w	9.912	15.147	8.058	8.129	7.177	7.293	5.066	5.174
E2-s-r	8.652	12.910	6.345	6.325	5.373	5.177	2.311	2.015
EE2-d-w	9.438	14.554	4.706	7.141	5.376	5.376	3.136	3.334
F1-d-w	11.066	15.214	9.175	13.330	8.321	8.302	6.232	6.232
F1-s-r	9.590	14.092	8.633	7.369	6.340	6.269	3.060	2.910
FF1-d-w	10.703	14.194	8.200	8.232	7.170	10.819	4.316	4.310
L-d-w	10.791	14.415	8.731	8.803	7.677	7.782	5.379	5.562
L-s-r	9.742	12.659	7.147	7.077	5.952	5.914	2.573	2.535
LL-d-w	10.242	13.512	7.718	7.775	6.448	6.459	3.347	3.355

c) Comparison of the orientation of O11 with respect to the plane.
The values written in red correspond to the cases in which O11 does not rotate off-plane.

Structure and conformer	Angle of O11 with the plane of the benzene ring							
	in vacuo		in chloroform		in acetonitrile		in water	
	input with O11 free to rotate	input with O11 frozen on the plane	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input	using *in vacuo* optimized input (O11 off-plane)	O11 on the plane in input
A-w [a]	0.000	–	0.000	–	0.000	–	0.000	–
A-r [a]	0.000	–	0.000	–	0.000	–	0.000	–
AA-w [a]	0.002	–	0.028	–	0.019	–	0.080	–
B-w	66.520	0.115	67.028	0.035	66.520	0.095	67.237	46.830
B-r	72.185	0.623	69.439	49.328	69.882	70.115	71.976	49.163
BB-w	63.738	0.003	64.229	0.079	64.037	44.651	62.977	43.386
D-w	73.475	0.017	73.929	0.017	77.753	0.010	76.026	75.929
D-r	79.242	0.726	77.629	77.913	86.851	–	76.524	76.428
DD-w	70.293	0.017	69.394	70.580	70.717	71.465	73.407	72.513
E1-w	73.845	0.056	74.915	77.257	77.753	89.642	76.090	76.060
E1-r	73.427	0.732	76.645	77.572	86.851	77.217	89.618	76.364
EE1-w	73.789	0.003	71.945	0.074	73.874	73.484	73.547	73.768
E2-w	63.523	13.466	61.251	64.599	60.188	64.301	61.655	65.729
E2-r	62.545	17.123	60.658	64.983	59.993	64.880	60.604	64.071
EE2-w	63.839	0.005	63.756	62.874	63.883	62.663	63.711	61.553
F1-w	73.981	0.029	74.959	0.012	78.419	86.102	79.033	78.759
F1-r	73.512	0.540	77.818	78.321	83.749	81.109	89.337	78.958
FF1-w	70.789	0.005	71.277	72.586	71.712	0.029	71.701	71.600
L-w	54.053	22.901	54.930	55.503	55.346	55.803	56.542	55.910
L-r	55.705	19.413	55.990	55.865	57.336	56.491	58.658	58.288
LL-w	52.310	22.455	53.197	53.404	53.413	53.274	53.006	53.302

[a] In this case, the angle was not frozen, because O11 remains on the plane on optimization after IHB removal, when R=H.