TABLE S 13. Comparison of the Results for the three Conformers of 2-hydroxybenzaldehyde.

The three conformers are denoted in the same way as in fig. 8: *a* is the conformer with the intramolecular H-bond; *b* is the conformer without the intramolecular H-bond and with the sp^2 O on the other side with respect to the OH; *c* is the conformer without the intramolecular H-bond and with the sp^2 O on the same side as the OH

a) Comparison of the HF/6-31G(d,p), MP2/6-31+G(d,p) and DFT/B3LYP/6-31++G(d,p) relative energies of the three conformers.

Method and conformers	Relative energy (kcal/mol)			
	in vacuo	in chloroform	in acetonitrile	in water
HF/6-31G(d,p)				
a	0.000	0.000	0.000	0.000
b	6.125	4.239	3.485	1.301
c	10.416	7.639	6.455	3.693
MP2/6-31+G(d,p)				
a	0.000	0.000	0.000	0.000
b	7.350	5.404	4.586	2.132
c	10.323	7.702	6.565	3.540
DFT/B3LYP /6-31++G(d,p)				
a	0.000	0.000	0.000	0.000
b	8.644	6.477	5.573	2.953
c	11.488	8.672	7.458	4.269

b) Comparison of the HF/6-31G(d,p), MP2/6-31+G(d,p) and DFT/B3LYP/6-31++G(d,p) results for the parameters of the intramolecular H-bond in conformer a.

Method and medium	H-bond parameters			Torsion angles of the atoms involved in the H-bond		∠O11 with the plane
	H···O Å	O···O Å	OĤO	H atom	O atom	
HF/6-31G(d,p)						
in vacuo	1.883	2.693	141.46	0.000	180.000	0.000
in chloroform	1.881	2.693	141.73	–0.005	–179.994	0.007
in acetonitrile	1.880	2.693	141.81	–0.007	–179.997	0.000
in water	1.891	2.700	141.17	0.061	179.984	0.014
MP2/6-31+G(d,p)						
in vacuo	1.802	2.672	145.80	–0.014	179.985	0.009
in chloroform	1.794	2.668	146.26	0.000	–179.997	0.011
in acetonitrile	1.790	2.666	146.42	0.002	–179.990	0.017
in water	1.804	2.674	145.54	–0.007	179.986	0.008
DFT/B3LYP /6-31++G(d,p)						
in vacuo	1.753	2.633	146.29	0.006	–179.992	0.006
in chloroform	1.749	2.632	146.72	–0.027	–179.991	0.021
in acetonitrile	1.732	2.638	147.04	–0.004	–179.986	0.012
in water	1.756	2.636	146.24	0.000	–179.987	0.017

c) Comparison of the HF/6-31G(d,p) and DFT/B3LYP/6-31++G(d,p) enthalpies (sum of electronic and thermal enthalpies) of the conformers without the IHB with respect to the enthalpy of the conformer with the IHB (taken as reference).

Method and conformers	Enthalpy difference (kcal/mol)			
	in vacuo	in chloroform	in acetonitrile	in water
HF/6-31G(d,p)				
a	0.000	0.000	0.000	0.000
b	5.801	3.910	3.153	0.833
c	10.008	7.281	6.115	3.242
DFT/B3LYP /6-31++G(d,p)				
a	0.000	0.000	0.000	0.000
b	8.441	6.268	5.355	2.538
c	11.236	8.459	7.253	3.886