Supplementary Information

Structure-Property Relationship in Selected Naphtho- and Anthraquinone Derivatives on the basis of Density Functional Theory and Car-Parrinello Molecular Dynamics

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14. **Figure S8.** A detailed view of the proton transfer event as shown by the time evolution of the distance parameters in the hydrogen bridges of compound **1** in the crystal. The upper lines: donor-acceptor distances r, the lower lines: the corresponding proton position parameters q (defined as q = rH^{BP}...O – r-OH^{BP})

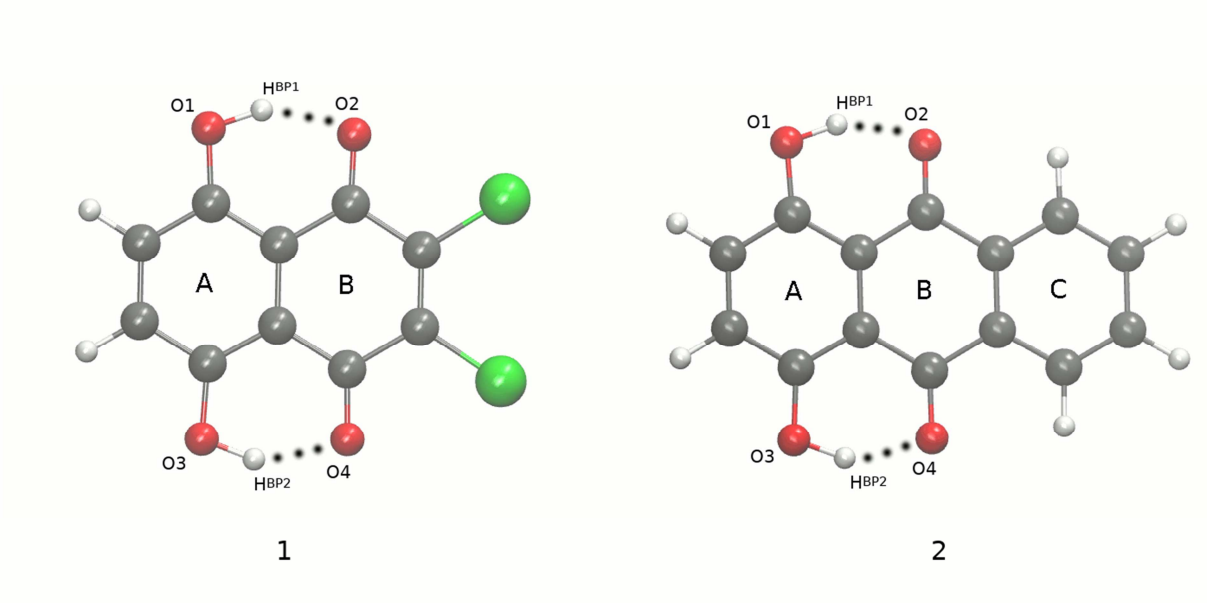


Figure S1. Molecular structures of 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone (**1**) [1] and 1,4-dihydroxy-anthraquinone (**2**) [2] with atoms numbering scheme prepared for the study. Only atoms of interest are indicated. Aromatic rings are indicated as well and the notation was used for HOMA aromaticity index.

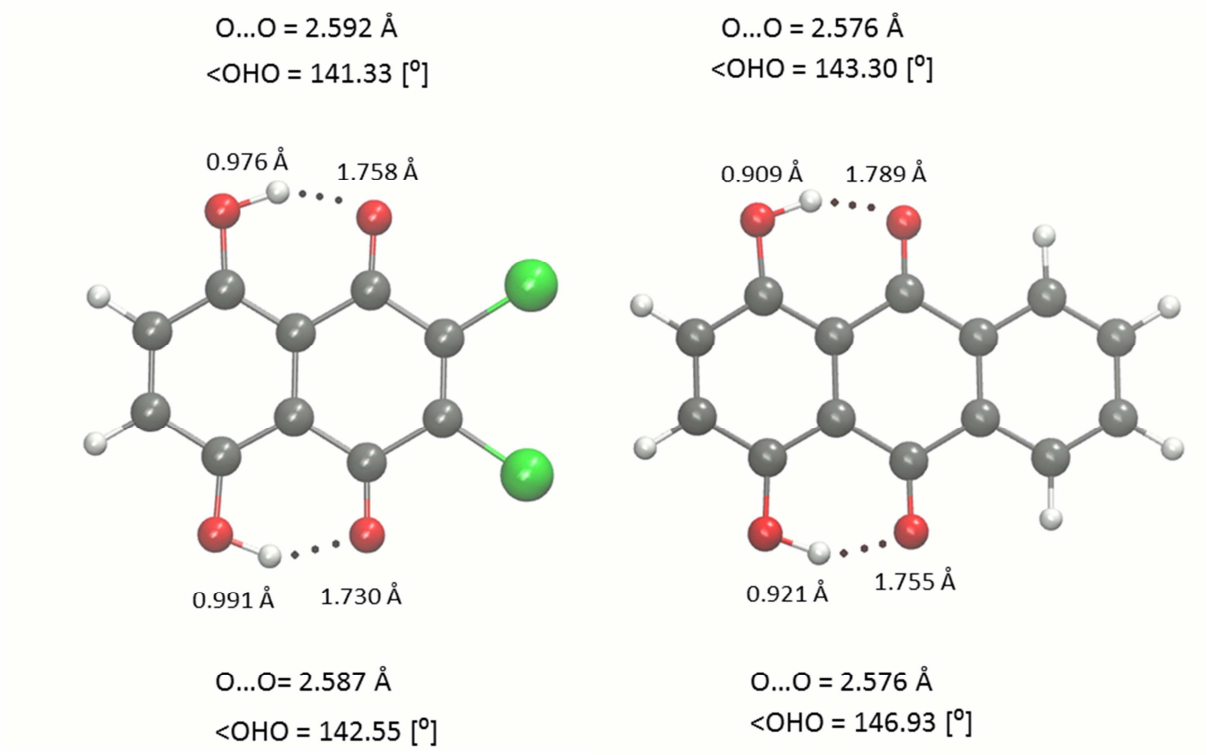


Figure S2. Experimental values (X-ray) of intramolecular hydrogen bonds present in the 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone (**1**) [1] and 1,4-dihydroxy-anthraquinone (**2**) [2]. Atoms coloring scheme: red –oxygen atom, grey – carbon atoms, green – chlorine atom, white – hydrogen atom.

Table S1. The intramolecular hydrogen bond metric parameters of 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone (only one intramolecular hydrogen bond was taken into account because of symmetry of the molecule). The simulations were performed at DFT level of theory with 6-311+G(2d,2p) basis set and various functionals for benchmarking as it is shown in the Table. The interatomic distances are given in [Å].

Metric parameters	**Functionals**		
	B3LYP [3]	**PBE [4]**	**ωB97XD [5]**
Simulations *in vacuo*			
O1…O2	**2.5705**	**2.5325**	**2.5794**
O1-H^{BP1}	**0.9887**	**1.0197**	**0.9798**
H^{BP1}...O2	**1.6877**	**1.5900**	**1.7131**
∠O1H^{BP1}O2 [º]	**146.47**	**151.36**	**145.26**
Simulations with solvent reaction field (PCM model and water as a solvent)			
O1…O2	**2.5701**	**2.5316**	**2.5796**
O1-H^{BP1}	**0.9887**	**1.0196**	**0.9797**
H^{BP1}...O2	**1.6851**	**1.5874**	**1.7121**
∠O1H^{BP1}O2 [º]	**146.80**	**151.68**	**145.45**

Table S2. The intramolecular hydrogen bond metric parameters of 1,4-dihydroxy-anthraquinone (only one intramolecular hydrogen bond was taken into account because of symmetry of the molecule). The simulations were performed at DFT level of theory with 6-311+G(2d,2p) basis set and various functionals for benchmarking as it is shown in the Table. The interatomic distances are given in [Å].

Metric parameters	**Functionals**		
	B3LYP [3]	**PBE [4]**	**ωB97XD [5]**
Simulations *in vacuo*			
O1…O2	**2.5569**	**2.5236**	**2.5654**
O1-H^{BP1}	**0.9903**	**1.0208**	**0.9812**
H^{BP1}...O2	**1.6664**	**1.5770**	**1.6909**
∠O1H^{BP1}O2 [º]	**147.38**	**151.89**	**146.26**
Simulations with solvent reaction field (PCM model and water as a solvent)			
O1…O2	**2.5497**	**2.5170**	**2.5591**
O1-H^{BP1}	**0.9915**	**1.0225**	**0.9822**
H^{BP1}...O2	**1.6536**	**1.5651**	**1.6798**
∠O1H^{BP1}O2 [º]	**148.08**	**152.55**	**146.83**

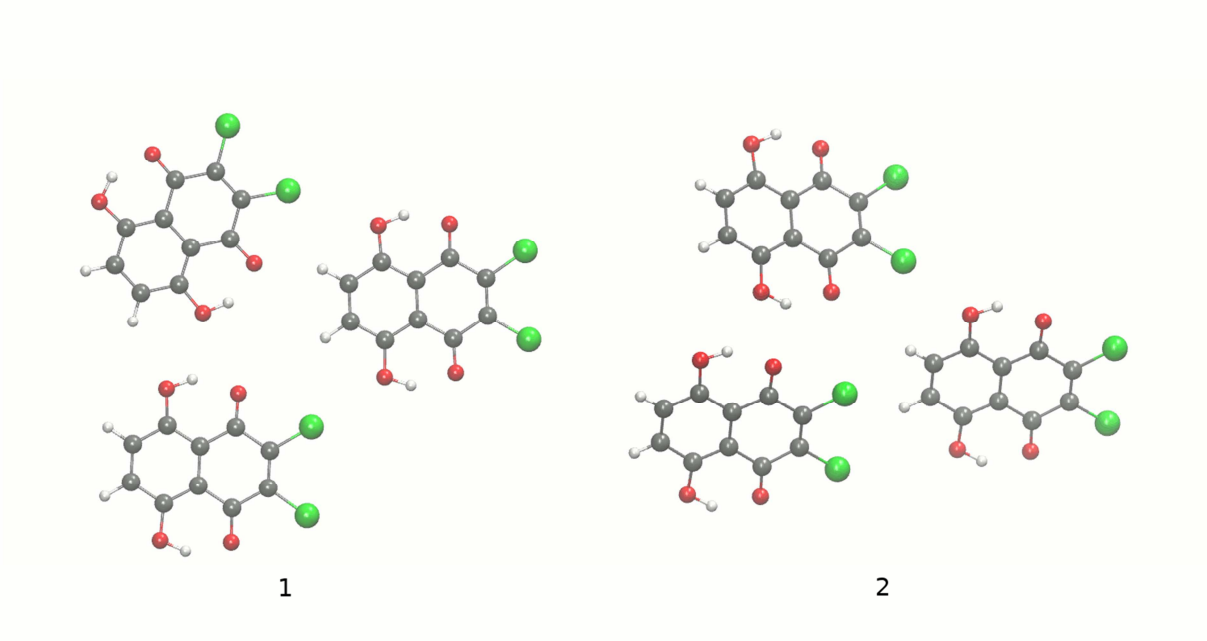


Figure S3. The comparison of calculated at the B3LYP/6-311+G(2d,2p) level of theory (left 1) and experimental – X-ray data (right 2) [1] structures of trimers of 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone.

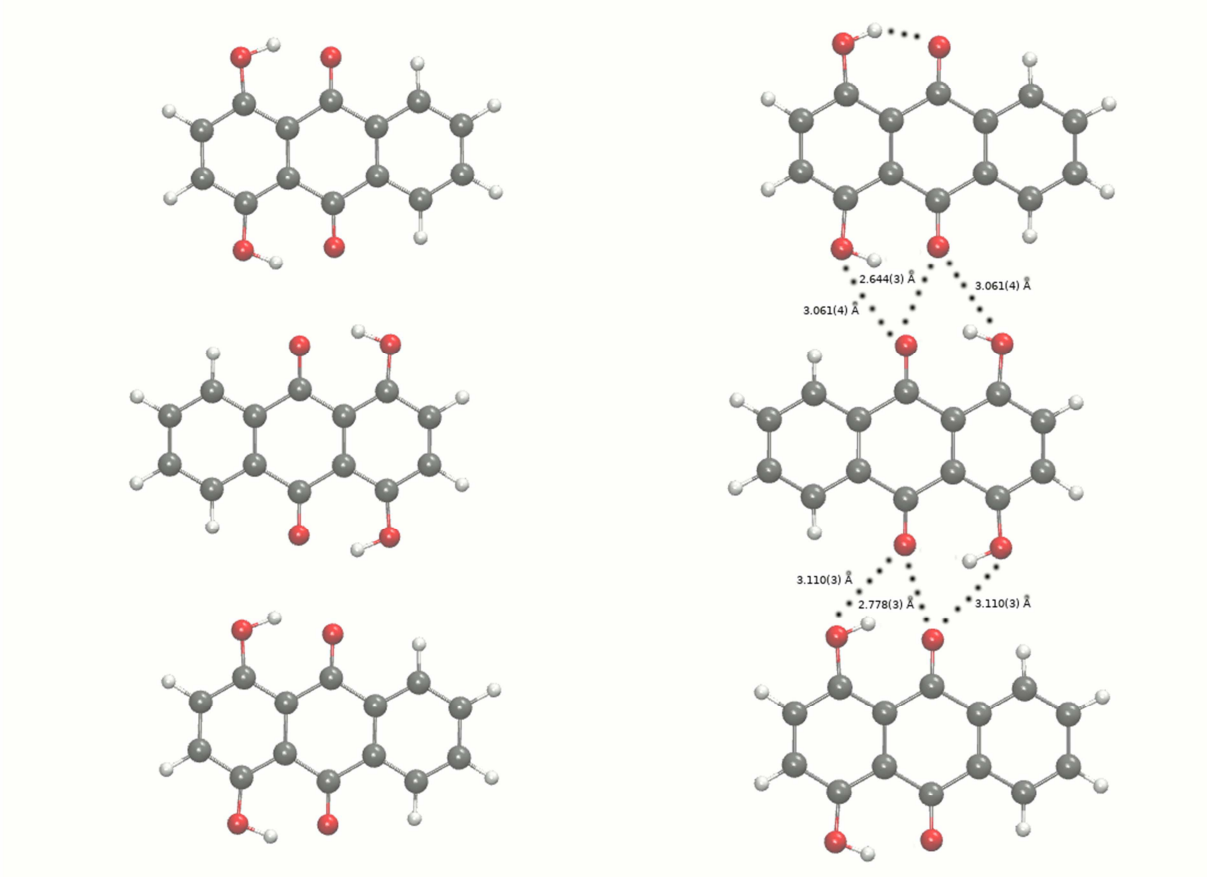


Figure S4. The comparison of calculated at the B3LYP/6-311+G(2d,2p) level of theory (left 1) and experimental – X-ray data (right 2) [2] structures of trimers of 1,4-dihydroxy-anthraquinone. The dotted lines indicate the shortest intermolecular contact distances.

Table S3. Computed values of HOMA aromaticity index for 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone. The simulations were performed at ωB97XD/6-311+G(2d,2p) level of theory in the gas phase and with PCM solvation model (water was used as a solvent). The structure of the compound with the rings indication is presented in Figure S1.

Structures	Rings	HOMA aromaticity index	
		Gas phase	Water
1	**A**	0.872	0.870
	B	-0.448	-0.398
2	**A**	0.860	0.859
	B	-0.396	-0.347
3	**A**	0.845	0.844
	B	-0.328	-0.280
4	**A**	0.820	0.820
	B	-0.242	-0.193
5	**A**	0.781	0.781
	B	-0.139	-0.090
6	**A**	0.726	0.727
	B	-0.043	0.005
7	**A**	0.665	0.666
	B	0.031	0.082
8	**A**	0.607	0.609
	B	0.086	0.141
9	**A**	0.554	0.556
	B	0.130	0.187
10	**A**	0.503	0.507
	B	0.164	0.223
11	**A**	0.457	0.460
	B	0.193	0.254
12	**A**	0.410	0.4152
	B	0.217	0.280
13	**A**	0.365	0.371
	B	0.237	0.300
14	**A**	0.321	0.327
	B	0.252	0.317
15	**A**	0.275	0.283
	B	0.265	0.332
16	**A**	0.228	0.237
	B	0.278	0.345

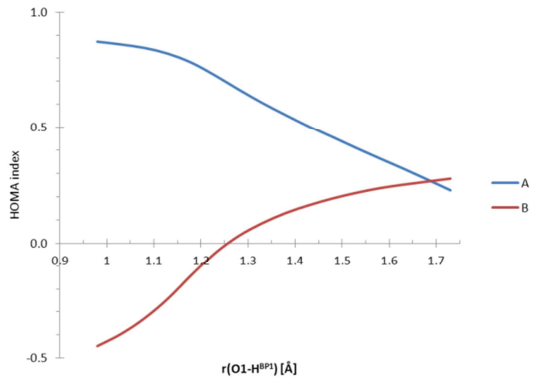
Table S4. Computed values of HOMA aromaticity index for 1,4-dihydroxy-anthraquinone. The simulations were performed at ωB97XD/6-311+G(2d,2p) level of theory in the gas phase and with PCM solvation model (water was used as a solvent). The structure of the compound with the rings indication is presented in Figure S1.

Structures	Rings	HOMA aromaticity index	
		Gas phase	Water
1	**A**	0.874	0.885
	B	-0.302	-0.264
	C	0.994	0.994
2	**A**	0.864	0.876
	B	-0.255	-0.217
	C	0.994	0.993
3	**A**	0.849	0.864
	B	-0.194	-0.157
	C	0.993	0.992
4	**A**	0.827	0.845
	B	-0.122	-0.086
	C	0.992	0.991
5	**A**	0.790	0.812
	B	-0.046	-0.013
	C	0.990	0.990
6	**A**	0.740	0.765
	B	0.016	0.046
	C	0.989	0.988
7	**A**	0.683	0.712
	B	0.059	0.088
	C	0.987	0.986
8	**A**	0.627	0.661
	B	0.087	0.117
	C	0.986	0.985
9	**A**	0.572	0.610
	B	0.108	0.135
	C	0.985	0.984
10	**A**	0.521	0.560
	B	0.123	0.150
	C	0.984	0.984
11	**A**	0.471	0.515
	B	0.134	0.161
	C	0.984	0.983

Table S4 (Continuation). Computed values of HOMA aromaticity index for 1,4-dihydroxy-anthraquinone. The simulations were performed at ωB97XD/6-311+G(2d,2p) level of theory in the gas phase and with PCM solvation model (water and ethanol were used as solvents). The structure of the compound with the rings indication is presented in Figure S1.

Structures	Rings	HOMA aromaticity index	
		Gas phase	Water
12	**A**	0.423	0.468
	B	0.144	0.171
	C	0.983	0.983
13	**A**	0.374	0.421
	B	0.151	0.178
	C	0.983	0.983
14	**A**	0.327	0.375
	B	0.157	0.182
	C	0.983	0.983
15	**A**	0.277	0.327
	B	0.160	0.185
	C	0.983	0.983
16	**A**	0.226	0.279
	B	0.162	0.186
	C	0.983	0.983

compound 1



compound 2

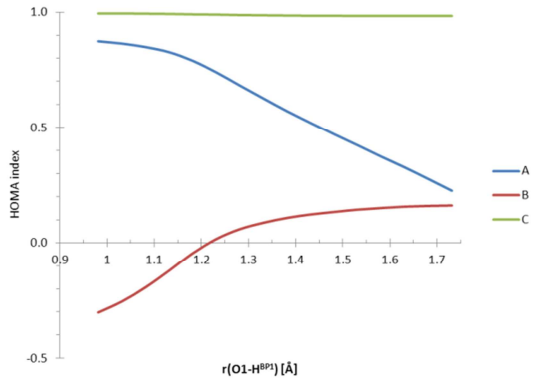


Figure S5. The evolution of the HOMA aromaticity index for the rings A, B, C (see Figure S1) as a function of the O1-H^{BP1} elongation.

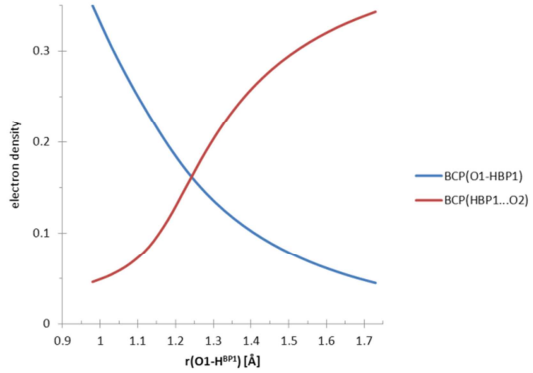
Table S5. The values of net atomic charges [e] computed according to AIM at ωB97XD/6-311+G(2d,2p) level of theory for the 2,3-dichloro-5,8-dihydroxy-1,4-naphthoquinone.

O1-H^{BP1} [Å]	**Proton-donor - O1 atom**	**H^{BP1}**	**Proton-acceptor - O2 atom**
0.9798	-1.171596	0.657689	-1.112432
1.0298	-1.156669	0.642683	-1.113748
1.0798	-1.145249	0.630364	-1.115879
1.1298	-1.142935	0.625849	-1.118221
1.1798	-1.147062	0.629388	-1.122833
1.2298	-1.150862	0.636901	-1.130134
1.2798	-1.151415	0.644799	-1.138691
1.3298	-1.149943	0.65284	-1.147477
1.3798	-1.147571	0.660232	-1.156036
1.4298	-1.144971	0.666258	-1.162862
1.4798	-1.142504	0.670211	-1.167252
1.5298	-1.140054	0.67201	-1.16935
1.5798	-1.137788	0.672196	-1.169478
1.6298	-1.135711	0.671005	-1.167992
1.6798	-1.133651	0.669031	-1.165496
1.7298	-1.131616	0.666532	-1.162542

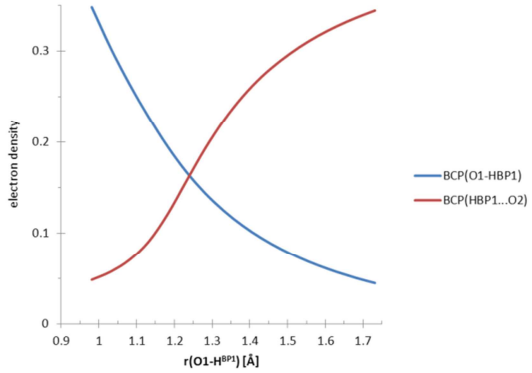
Table S6. The values of net atomic charges [e] computed according to AIM at ωB97XD/6-311+G(2d,2p) level of theory for the 1,4-dihydroxy-anthraquinone.

O1-H^{BP1} [Å]	**Proton-donor - O1 atom**	**H^{BP1}**	**Proton-acceptor - O2 atom**
0.9812	-1.177572	0.657309	-1.13562
1.0312	-1.162958	0.642173	-1.136548
1.0812	-1.15288	0.630074	-1.137724
1.1312	-1.151144	0.625636	-1.139305
1.1812	-1.155387	0.628703	-1.14276
1.2312	-1.159507	0.635267	-1.148654
1.2812	-1.160815	0.643168	-1.156035
1.3312	-1.160154	0.65104	-1.164011
1.3812	-1.158478	0.658691	-1.171967
1.4312	-1.156524	0.664978	-1.178475
1.4812	-1.154515	0.668849	-1.182494
1.5312	-1.152369	0.670781	-1.184533
1.5812	-1.150359	0.67103	-1.184606
1.6312	-1.148454	0.669855	-1.183141
1.6812	-1.146522	0.668331	-1.18077
1.7312	-1.144638	0.665984	-1.1778

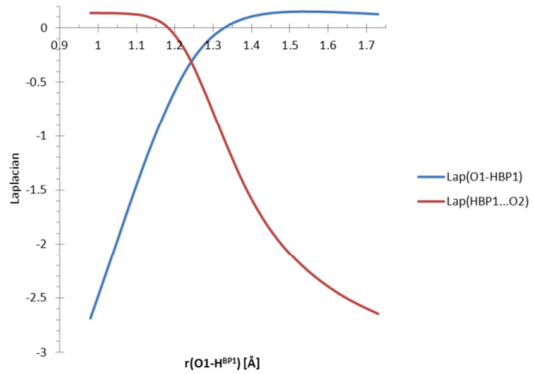
compound 1, ρ at the BCP(O1-H^{BP1})



compound 2, ρ at the BCP(O1-H^{BP1})



compound 1, Laplacian of ρ at the BCP(O1-H^{BP1})



compound 2, Laplacian of ρ at the BCP(O1-H^{BP1})

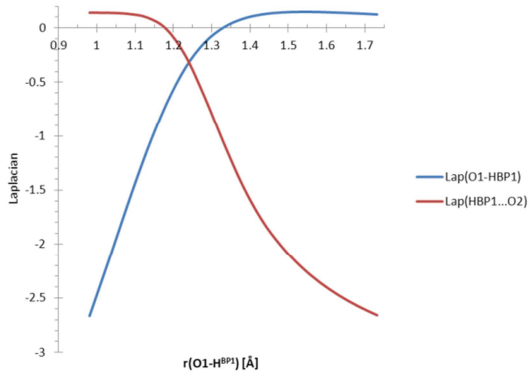


Figure S6. Dependence of the electron density (ρ) (upper graphs) and its Laplacian (lower graphs) at selected BCPs on the donor O1 – proton H^{BP1} distance for the studied compounds **1** and **2**.

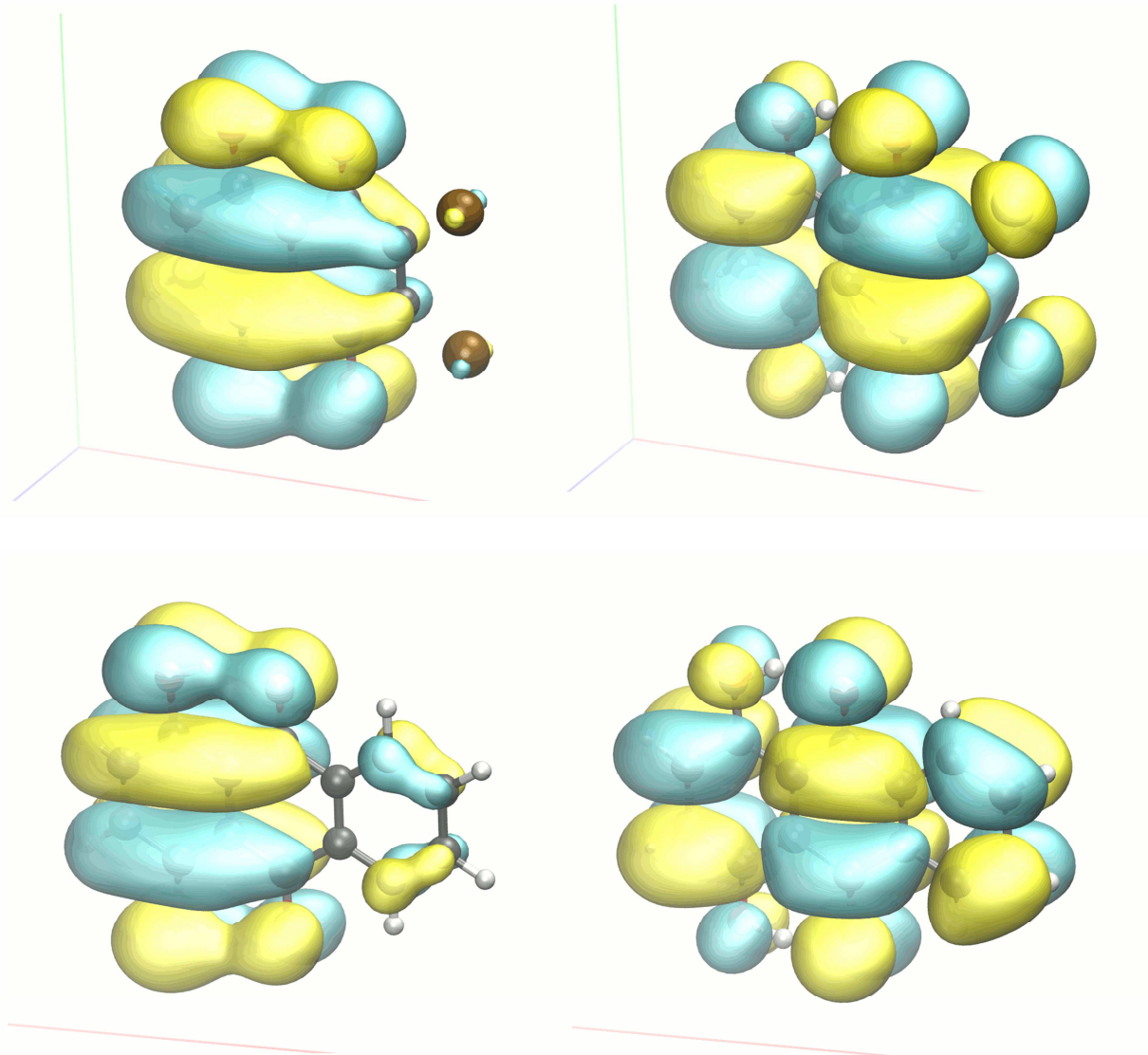


Figure S7. The isosurfaces of the HOMO (left column) and LUMO (right column) orbitals of the compounds **1** (upper row) and **2** (lower row). The calculations were carried out using B3LYP/6-311+G(2d,2p) level of theory in the gas phase. The differences with the shapes of the orbitals when ωB97XD functional was used, or solvent effects included - are negligible. The isosurfaces were drawn for the value of 0.01.

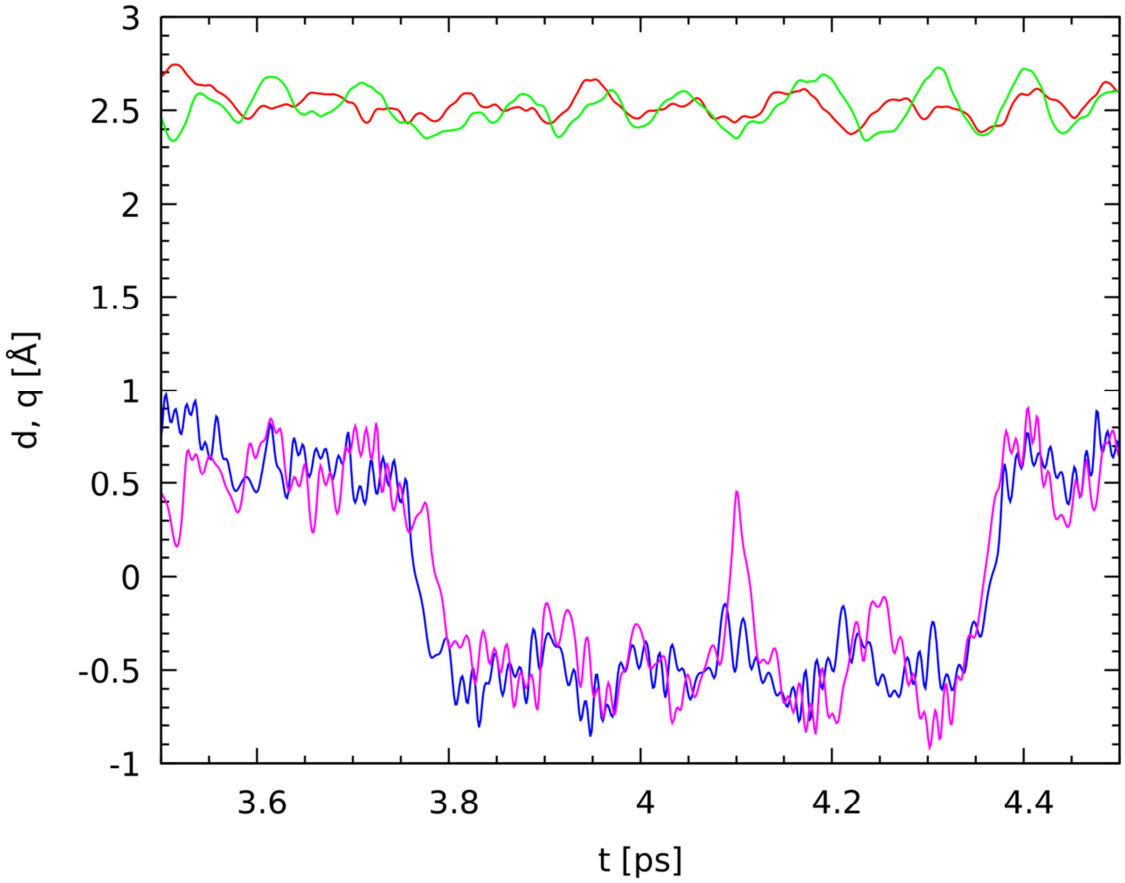


Figure S8. A detailed view of the proton transfer event as shown by the time evolution of the distance parameters in the hydrogen bridges of compound **1** in the crystal. The upper lines: donor-acceptor distances r, the lower lines: the corresponding proton position parameters q (defined as q = rH^{BP}...O – rO-H^{BP}). Color coding is as follows: red - r(O1...O2), green - r(O3...O4), blue - q(O1-H^{BP1}-O2), violet - q(O3-H^{BP2}-O4).

References:

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