Supporting Information: H-Bond Isomerization in Crystalline Cellulose III_I: Proton Hopping versus Hydroxyl Flip-Flop

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FHI-aims unit cell relaxation and energy evaluation The first principles calculations were carried out with the FHI-aims all-electron code.[1] The self-consistency cycle accuracy were set to 10^{-5} [e], 10^{-4} [eV] and 10^{-6} [eV] for the electron density, electronic eigenvalues and total energy change for calculations in `tier1` and `tier2` basis sets. The geometry and cell relaxations were carried out using `trm` algorithm and residual force component threshold of 10^{-3} eV/Å. The periodic calculations used converged `k-grid` of `6x6x6`. Phonon evaluations using harmonic approximation on PBE+vdW[2,3] potential-energy surface were performed on `2x2x2` supercell with `k-grid` of `3x3x3` and `q-points` of 3. The `phonopy`[4] wrapper generated 252 disturbed structures.

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aimsChain transition path search Transition path calculations were carried out with the `aimsChain` tool in combination with the FHI-aims code. The string method[5] on the PBE+vdW[2,3] potential-energy surface has been used for the path optimization. We used the unit cell parameters of structure B for each point along the path. The proton-hopping path was optimized using 10 interpolating images with a force threshold of 0.2 eV/Å, and the transition state was further refined using the climbing image technique with 0.05 eV/Å threshold for the forces. For the flip-flop mechanisms, which is characterized by structurally more complicated transition paths, we used 20 images for each optimized path. We also used tighter criteria of 0.15 eV/Å for initial path optimization, followed by 0.05 eV/Å climbing image threshold. In the case of A→P transition via long angles, we were not able to converge the transition state search to the specified accuracy. Instead we used the most converged path with a residual force of 0.065 eV/Å. Please note that structures A, P, and B were optimized at PBE+vdW level of theory and some close structures might have a somewhat lower single-point energy when evaluated using different functionals.

Structures and paths In the following tables we specify the calculated potential energies of various paths connecting structures A, P and B. We report here only relative energies and relaxed geometries of A, P and B at PBE+vdW level of theory, whereas the complete calculations have been deposited in the NOMAD repository (`http://nomad-repository.eu`, DOI: 10.17172/NOMAD/2015.11.19-1).

Table 1: Proton hopping mechanism, calculated transition paths energies. The energies are given in kcal/mol per H-bond chain

	A→P			P→B		
#	PBE+vdW	PBE+MBD	PBE0+MBD	PBE+vdW	PBE+MBD	PBE0+MBD
1	0.96	0.85	1.09	0.49	0.44	0.56
2	1.00	0.89	1.21	0.54	0.49	0.69
3	1.20	1.08	1.57	0.75	0.68	1.06
4	1.89	1.75	2.67	1.44	1.35	2.18
5	2.44	2.21	3.53	2.03	1.85	3.08
6	4.53	4.28	6.59	4.01	3.81	6.00
7	2.67	2.48	4.00	2.23	2.09	3.53
8	2.20	2.09	3.31	1.70	1.64	2.74
9	1.11	1.03	1.70	0.62	0.59	1.15
10	0.70	0.63	1.05	0.21	0.19	0.49
11	0.54	0.48	0.73	0.05	0.04	0.17
12	0.49	0.44	0.56	0.00	0.00	0.00

Table 2: OH flip-flop mechanism 1: rotation around two small angles. Calculated transition paths energies at different level of theory. The energies are given in kcal/mol per H-bond chain

	A→P			P→B		
#	PBE+vdW	PBE+MBD	PBE0+MBD	PBE+vdW	PBE+MBD	PBE0+MBD
1	0.96	0.85	1.07	0.50	0.44	0.55
2	1.16	1.04	1.13	0.62	0.52	0.54
3	1.88	1.72	1.59	0.91	0.78	0.71
4	3.08	2.88	2.53	1.64	1.54	1.26
5	4.03	3.81	3.33	2.75	2.64	2.19
6	4.24	4.00	3.57	3.76	3.67	3.09
7	5.23	4.99	4.51	4.25	4.15	3.59
8	6.99	6.74	6.08	5.38	5.28	4.68
9	7.13	6.89	6.19	6.54	6.41	5.71
10	6.84	6.61	5.93	6.91	6.78	5.98
11	5.84	5.63	5.02	6.71	6.59	5.81
12	5.12	4.89	4.38	6.37	6.32	5.55
13	5.19	4.95	4.46	5.62	5.59	4.92
14	5.30	5.06	4.49	5.67	5.61	4.90
15	5.96	5.79	5.13	6.37	6.28	5.45
16	6.81	6.70	5.95	6.82	6.76	5.87
17	6.87	6.76	5.98	6.68	6.60	5.69
18	5.58	5.47	4.76	5.52	5.42	4.59
19	3.28	3.19	2.69	3.55	3.47	2.79
20	1.55	1.45	1.19	1.76	1.69	1.22
21	0.80	0.71	0.62	0.74	0.67	0.39
22	0.53	0.46	0.51	0.19	0.13	0.02
23	0.49	0.44	0.56	0.00	0.00	0.00

Table 3: OH flip-flop mechanism 2: OH2 around small angle and OH6 around large. Calculated transition paths energies at different level of theory. The energies are given in kcal/mol per H-bond chain

	A→P			P→B		
#	PBE+vdW	PBE+MBD	PBE0+MBD	PBE+vdW	PBE+MBD	PBE0+MBD
1	0.96	0.85	1.07	0.49	0.44	0.56
2	0.98	0.88	1.13	0.62	0.58	0.78
3	1.21	1.10	1.26	0.60	0.57	0.77
4	1.76	1.63	1.69	0.75	0.70	0.83
5	2.96	2.80	2.72	0.91	0.82	0.90
6	4.90	4.71	4.50	1.48	1.35	1.35
7	6.66	6.46	6.22	3.28	3.13	2.92
8	8.01	7.80	7.47	5.48	5.33	5.00
9	8.98	8.73	8.24	7.10	6.92	6.54
10	9.20	8.94	8.36	8.33	8.13	7.61
11	9.10	8.83	8.19	8.85	8.60	7.90
12	8.01	7.77	7.07	7.95	7.71	6.91
13	6.39	6.21	5.53	6.26	6.08	5.29
14	4.51	4.37	3.78	4.34	4.22	3.52
15	2.68	2.56	2.11	2.53	2.41	1.89
16	1.42	1.31	1.03	1.14	1.04	0.70
17	0.83	0.74	0.63	0.52	0.47	0.23
18	0.58	0.49	0.50	0.13	0.11	-0.03
19	0.51	0.44	0.59	0.03	0.03	0.01
20	0.59	0.53	0.75	0.08	0.08	0.14
21	0.55	0.50	0.69	0.07	0.08	0.15
22	0.52	0.46	0.55	0.00	0.00	0.00
23	0.49	0.44	0.56			

Table 4: OH flip-flop mechanism 3: OH2 around large angle and OH6 around small. Calculated transition paths energies at different level of theory. The energies are given in kcal/mol per H-bond chain

	A→P			P→B		
#	PBE+vdW	PBE+MBD	PBE0+MBD	PBE+vdW	PBE+MBD	PBE0+MBD
1	0.96	0.85	1.07	0.49	0.44	0.56
2	0.98	0.89	1.16	0.64	0.60	0.80
3	1.27	1.20	1.50	1.00	0.96	1.12
4	2.98	2.95	2.95	2.37	2.33	2.22
5	5.60	5.57	5.31	5.06	5.09	4.65
6	7.17	7.10	6.79	6.44	6.44	5.95
7	7.67	7.57	7.29	6.77	6.71	6.22
8	7.42	7.32	7.05	7.07	7.02	6.46
9	7.25	7.16	6.87	7.39	7.32	6.67
10	7.52	7.40	6.93	7.59	7.49	6.74
11	8.38	8.27	7.56	7.18	7.09	6.31
12	9.33	9.23	8.35	6.11	6.04	5.31
13	9.50	9.41	8.50	5.73	5.68	4.96
14	9.38	9.32	8.42	6.52	6.49	5.65
15	8.25	8.26	7.40	6.47	6.42	5.54
16	6.32	6.36	5.58	4.89	4.84	4.07
17	4.05	4.11	3.63	2.60	2.56	2.00
18	2.43	2.43	2.13	1.11	1.08	0.73
19	1.67	1.64	1.48	0.39	0.38	0.18
20	1.07	1.04	0.98	0.05	0.04	-0.03
21	0.66	0.61	0.63	0.00	0.00	0.01
22	0.51	0.45	0.56	0.00	0.00	0.00
23	0.49	0.44	0.56			

Table 5: OH flip-flop mechanism 4: rotation around two large angles. Calculated transition paths energies at different level of theory. The energies are given in kcal/mol per H-bond chain

	A→P			P→B		
#	PBE+vdW	PBE+MBD	PBE0+MBD	PBE+vdW	PBE+MBD	PBE0+MBD
1	0.96	0.85	1.07	0.49	0.44	0.56
2	0.96	0.86	1.09	0.63	0.61	0.78
3	4.34	4.35	4.04	3.25	3.27	3.03
4	7.62	7.51	7.16	6.38	6.39	5.95
5	7.99	7.91	7.52	6.93	6.90	6.47
6	8.09	7.99	7.49	7.26	7.22	6.71
7	8.33	8.28	7.75	7.41	7.36	6.81
8	9.40	9.36	8.84	8.46	8.53	7.93
9	10.54	10.64	10.03	9.30	9.50	8.84
10	9.61	9.60	9.04	8.39	8.60	7.97
11	9.17	9.21	8.55	7.18	7.39	6.81
12	8.85	8.81	8.07	7.26	7.44	6.84
13	8.04	7.89	7.17	7.29	7.46	6.82
14	6.14	5.95	5.21	6.60	6.72	6.06
15	3.73	3.61	2.99	6.22	6.23	5.59
16	0.87	0.79	0.64	5.41	5.32	4.73
17	0.59	0.51	0.51	3.52	3.41	3.02
18	0.60	0.51	0.68	1.82	1.75	1.70
19	0.61	0.52	0.70	1.08	0.99	0.83
20	0.65	0.57	0.78	0.32	0.28	0.15
21	0.70	0.65	0.86	0.01	0.00	-0.02
22	0.59	0.54	0.60	0.00	0.00	0.00
23	0.49	0.44	0.56			

Table 6: Pattern A

lattice_vector	4.42995483	0.16141875	0.01114836
lattice_vector	-1.81055781	7.40509444	-0.00465012
lattice_vector	-0.04499274	-0.00013944	10.36835151
C	1.33020425	4.17299699	4.17517727
C	1.80922844	5.24389972	3.19191501
C	1.21223090	5.02701774	1.79121122
C	1.37953396	3.54848254	1.37512969
C	0.94379873	2.57229169	2.47594900
C	1.25326851	1.11531815	2.12560215
C	1.22863801	3.39108251	9.35907635
C	0.75861203	2.31988886	8.37185162
C	1.36653612	2.53701549	6.97596983
C	1.20260932	4.01549971	6.55846256
C	1.62884029	4.99179334	7.66288894
C	1.32159961	6.44852658	7.30996471
O	1.60240678	6.54571945	3.71444910
O	1.89415637	5.92502562	0.92301102
O	0.60880361	3.22337836	0.20321102
O	1.68550421	2.88027367	3.66577708
O	1.15713039	0.29936623	3.29484752
O	0.96278355	1.01838216	8.89636623
O	0.69190829	1.63880665	6.10230305
O	1.98395361	4.34067972	5.39354574
O	0.87737873	4.68369461	8.84662052
O	1.41020022	7.26484419	8.47958780
H	0.23121635	4.21629139	4.31962460
H	2.90154746	5.11786349	3.10641529
H	0.12882840	5.25644713	1.79887885
H	2.44894852	3.37478726	1.15616124
H	-0.13883811	2.67998161	2.68905319
H	0.58680891	0.75816057	1.32848793
H	2.28753044	1.03408238	1.75268324
H	2.32629006	3.34802092	9.51343102
H	-0.33310969	2.44489505	8.27766586
H	2.44983917	2.30779553	6.99227201
H	0.13514648	4.18904221	6.32999538
H	2.70974055	4.88458346	7.88486265
H	1.99322606	6.80540500	6.51705727
H	0.28974369	6.52953645	6.93036567
H	0.66727757	6.89773518	3.53771661
H	1.12927250	1.65616887	5.22227813
H	0.24426217	-0.12503038	3.38433522
H	1.89873256	0.66614710	8.72431529
H	1.46470638	5.90694906	0.03909477
H	2.32254268	7.68933016	8.57437084

Table 7: Pattern P

lattice_vector	4.41670494	0.16508650	0.00720045
lattice_vector	-1.81240985	7.42221034	-0.00240995
lattice_vector	-0.05965352	0.00061772	10.37235309
C	1.32002968	4.20428809	4.20021689
C	1.78204031	5.27959918	3.21851577
C	1.20649764	5.04564594	1.80982435
C	1.38024666	3.56904359	1.39544175
C	0.93861862	2.60291067	2.50180844
C	1.21871096	1.14185135	2.16311820
C	1.20995126	3.41540738	9.38274868
C	0.73565044	2.34775415	8.39376125
C	1.33297570	2.56902233	6.99389696
C	1.18027697	4.05118920	6.58284666
C	1.60551876	5.02283567	7.69220106
C	1.29523447	6.48078664	7.34534604
O	1.44595880	6.55885730	3.74035317
O	1.89305245	5.94691080	0.94874072
O	0.60932014	3.24078419	0.22381104
O	1.68277438	2.91359940	3.69007241
O	0.99241919	0.34459260	3.33295968
O	0.94093605	1.04402090	8.91195556
O	0.63774111	1.68254923	6.12287403
O	1.96832917	4.37620996	5.42113516
O	0.85439309	4.70890339	8.87417536
O	1.38235589	7.29411049	8.51695839
H	0.22093729	4.24130719	4.34236387
H	2.87983880	5.20270931	3.14773860
H	0.12277435	5.27190961	1.80973354
H	2.44911647	3.39263515	1.17759603
H	-0.14242322	2.72294356	2.71580548
H	0.56955699	0.81149741	1.33967268
H	2.26289556	1.01667295	1.83346195
H	2.30799375	3.37412087	9.53286131
H	-0.35634501	2.47353685	8.30659853
H	2.41361186	2.32765281	6.99669640
H	0.11498833	4.23130544	6.35021964
H	2.68637334	4.91696948	7.91393448
H	1.96693306	6.84184119	6.55451587
H	0.26371697	6.56083199	6.96460710
H	0.03267720	7.26585434	3.52219226
H	1.05905839	1.70440099	5.23540810
H	-0.35905709	-0.42792833	3.57590652
H	1.87772828	0.69114012	8.74518398
H	1.46122282	5.94111759	0.06621178
H	2.29112796	7.72862464	8.60522637

Table 8: Pattern B

lattice_vector	4.38180933	0.14462593	0.01060351
lattice_vector	-1.91820678	7.48345080	-0.01332377
lattice_vector	-0.03953462	0.01223422	10.37465406
C	1.24492005	4.22100505	4.21336826
C	1.69088393	5.29925327	3.22781267
C	1.13918606	5.04487776	1.81315365
C	1.32741083	3.56572529	1.41099028
C	0.90263095	2.60183161	2.52600106
C	1.21107857	1.14348909	2.20046533
C	1.16586385	3.42109656	9.40146606
C	0.72759000	2.34035138	8.41519851
C	1.28919927	2.59152020	7.00389008
C	1.10396160	4.06969163	6.59679365
C	1.52014529	5.03638674	7.71263525
C	1.21314569	6.49371382	7.38148904
O	1.32308345	6.57601782	3.73422514
O	1.83787009	5.94215755	0.95614247
O	0.55626933	3.21753621	0.24408806
O	1.64007657	2.93655292	3.71087240
O	0.99685201	0.35284888	3.37755411
O	1.09247612	1.06494662	8.92718136
O	0.59683008	1.69210653	6.14402482
O	1.88442170	4.41506527	5.43520816
O	0.77421490	4.70423600	8.89296560
O	1.42047674	7.28748086	8.55774975
H	0.14466024	4.23288233	4.35015113
H	2.79090627	5.24503376	3.17027705
H	0.05485859	5.26684665	1.79233300
H	2.39738324	3.40079852	1.18999527
H	-0.18054001	2.70470608	2.73848819
H	0.57040966	0.79413245	1.37807068
H	2.25826422	1.03597207	1.87444609
H	2.26502820	3.40971352	9.54687868
H	-0.37201439	2.39389003	8.34974964
H	2.37363692	2.36961276	6.99129787
H	0.03573909	4.23394900	6.36697657
H	2.60181324	4.93462852	7.93315737
H	1.85832820	6.84112418	6.56180124
H	0.16774982	6.59996278	7.04933337
H	2.11850247	7.18695211	3.59467622
H	1.02389823	1.69523622	5.25948653
H	1.83800227	-0.17607879	3.54294402
H	0.29758466	0.45381308	8.78539607
H	1.41756627	5.93661578	0.06839235
H	0.57825328	7.81653873	8.71731985

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