Supporting Information

For

Performance of DFTB in comparison to ab initio and first principles methods for isomer geometries and energies of glucose epimers in vacuo and solution

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Page S10. Cartesian coordinates and energies of the structures studied in Figure S3 in xyz format, extracted using OpenBabel. The units of given are in Hartree for energy Angstrom for distance for the following structures:

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- **2.** B3LYP/6-311++G(d,p)-optimized geometry of allose, β-gg-(g+), 'rrrr'
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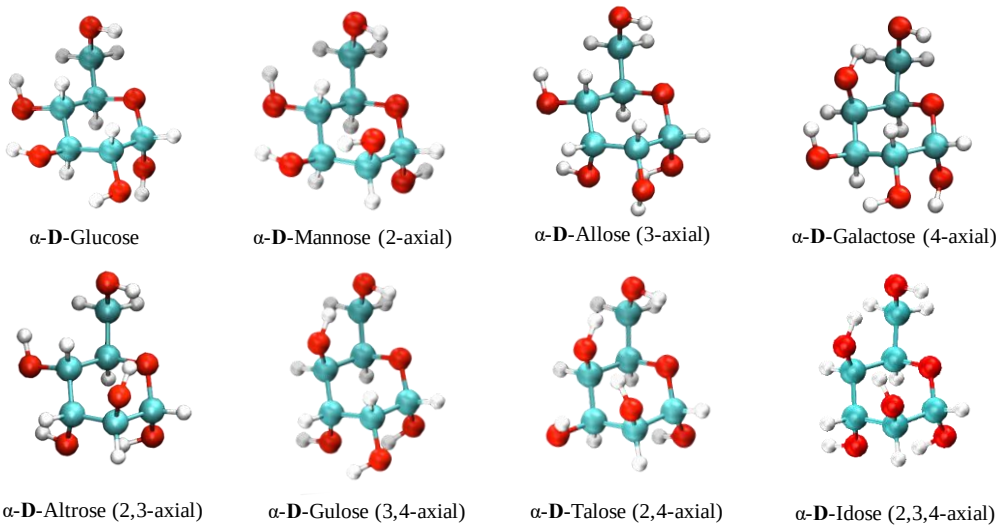


Figure S1. The ball and stick representation of α-**D**-aldopyranoses based on B3LYP-optimized structures in the gas phase.

Table S1. The number of initial structures from ref. 19, optimized at the B3LYP/6-311++G(d,p) level of theory in the gas and aqueous phase.

Epimer	Initial vacuum structures			Initial solvated structures		
	α	β	Total	α	β	Total
Glucose	15	15	30	15	15	30
Mannose	13	14	27	12	14	26
Allose	18	16	34	18	15	33
Galactose	20	25	45	10	8	18
Altrose	22	20	42	16	26	42
Gulose	16	16	32	16	16	32
Talose	9	9	18	9	9	18
Idose	13	14	27	13	14	27
Overall	126	129	255	109	117	226

Table S2. The number of optimized structures retaining the initial B3LYP conformation in both DFTB2 and DFTB3 methods and evaluated in the current work.

Epimer	Optimized vacuum structures			Optimized solvated structures		
	α	β	Total	α	β	Total
Heavy Atoms only						
Glucose	12	12	24	15	14	29
Mannose	10	12	22	12	13	25
Allose	16	14	30	18	14	31
Galactose	20	25	45	10	8	18
Altrose	19	17	36	16	25	41
Gulose	16	16	32	16	16	32
Talose	9	9	18	9	9	18
Idose	13	14	27	13	14	27
Overall	115	119	234	109	113	221
All Atoms						
Glucose	11	10	21	15	7	22
Mannose	10	10	20	12	13	25
Allose	8	7	15	10	4	14

Galactose	19	22	42	10	8	18
Altrose	19	11	30	16	13	39
Gulose	7	10	17	13	0	13
Talose	5	3	8	1	6	7
Idose	8	10	18	12	12	24
Overall	87	83	170	89	63	152

***Ab initio* and first principles single point isomer energies between large and small basis sets.**

Single point energy calculations for both α and β conformations at B3LYP/6-311++G** geometries have been performed using G3B3, HF/G3Large, MP2/G3Large, QCISD(T,FC)/6-31G(d), B3LYP/6-311++G(d,p), PBE/6-311++G(d,p), B3LYP/STO-3G, and PBE/STO-3G. Single point energies from each level of theory were compared against G3B3 as reference in Figure S1. To differentiate the energies between different methods, we define here $\Delta\Delta E_{isomer}$ as the relative isomer energy difference of α and β conformations relative to the lowest G3B3 energy isomer in both gas phase and water, β–talose, in each method against referenced G3B3 energies. Compared to DFT with large basis set, DFT with a minimal basis set deviates considerably from reference G3B3 energies. The structures studied in this analysis could be found below Figure S2, Structures 1 to 32.

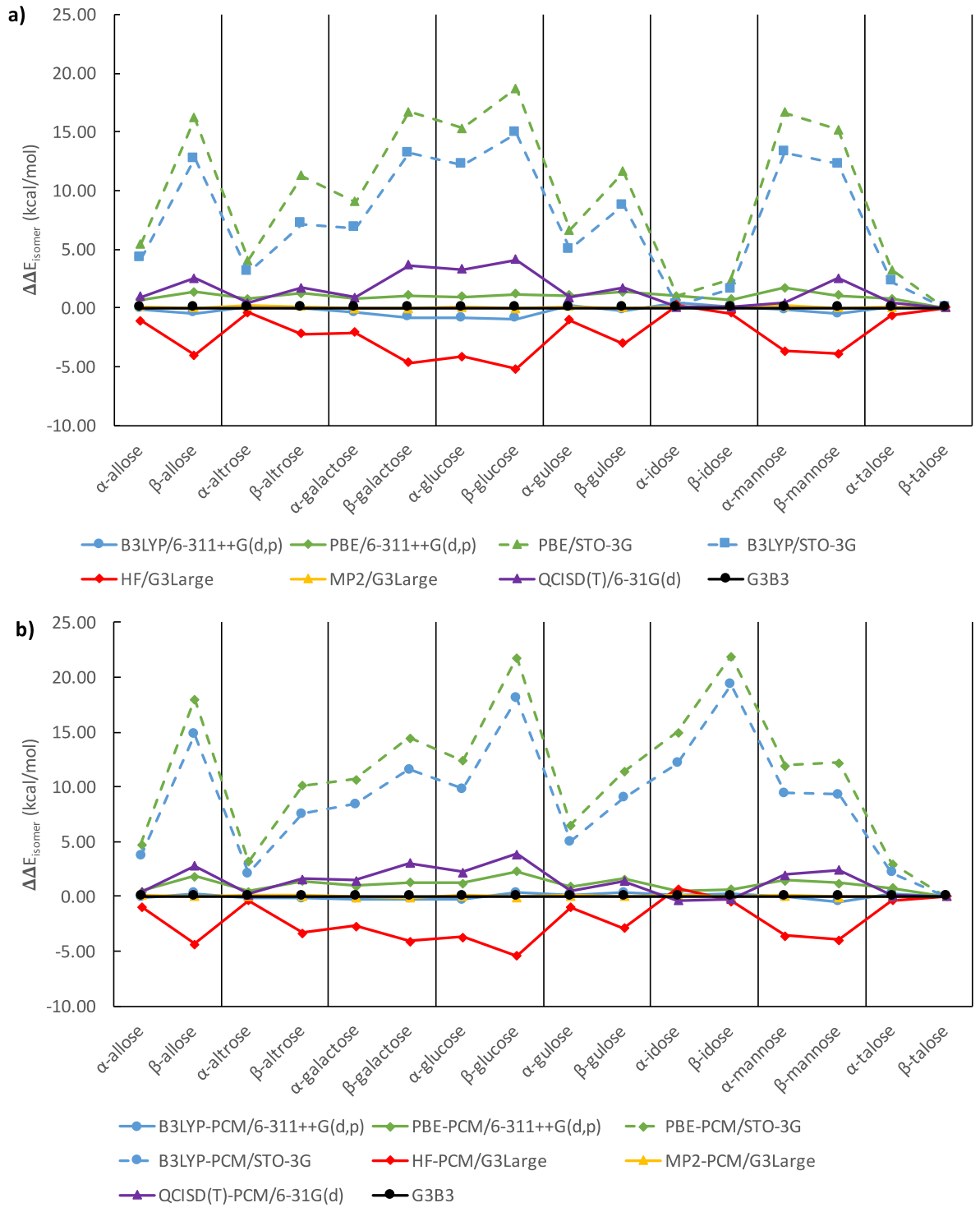


Figure S2. Comparison of relative isomer energies relative to the lowest G3B3 energy isomer, β–talose, and relative to G3B3 energies ($\Delta\Delta E_{isomer}$) in both a) vacuum and b) implicit solvent. Dashed lines represent STO-3G energies.

Structure 1: B3LYP/6-311++G(d,p)-optimized geometry of allose, α-tg-(g-), 'cOcc'

24
Energy: -687.0555034

C	-0.62296	-0.47902	-0.78380
C	-0.36702	0.99851	-1.09446
C	1.11626	1.33811	-0.92781
C	1.61472	0.90909	0.46905
C	-0.01647	-0.86348	0.57853
C	-0.04108	-2.37085	0.83299
H	1.67993	0.75873	-1.66351
H	-0.58283	-0.35756	1.37216
H	-0.14464	-1.08546	-1.56657
H	-0.68133	1.22088	-2.12049
H	2.69873	0.99674	0.53294
H	0.44558	-2.58889	1.78709
H	0.51048	-2.88690	0.04392
H	0.93867	3.24489	-0.56665
H	-2.01924	1.50015	-0.18453
H	-2.22798	-1.52659	-0.42852
H	-1.75707	-2.85416	1.68642
H	0.15051	1.87189	1.30142
O	1.35840	-0.48865	0.63830
O	-2.03797	-0.65497	-0.80882
O	-1.10984	1.82948	-0.18451
O	1.39810	2.69498	-1.21283
O	-1.38402	-2.88572	0.79988
O	1.08452	1.69626	1.50032

Structure 2: B3LYP/6-311++G(d,p)-optimized geometry of allose, β-gg-(g+), 'rrrr'

24
Energy: -687.0552428

C	-1.05192	-0.51739	-0.62701
C	-0.88265	0.99593	-0.80755
C	0.58445	1.41248	-0.72578
C	1.22691	0.84054	0.53536
C	-0.26452	-1.03069	0.59800
C	-0.19147	-2.55169	0.66235
H	1.12998	1.00397	-1.58668
H	-0.73882	-0.65289	1.51466
H	-0.67050	-1.02957	-1.51356
H	-1.28805	1.29441	-1.78204
H	-1.20237	-2.95976	0.62918
H	-2.84430	-0.16996	0.02036
H	0.27661	-2.84379	1.61136

H	1.39226	-2.70440	-0.44653
H	0.74228	1.24987	1.43361
H	3.00161	0.89025	1.32009
H	1.52484	3.11905	-0.59525
H	-1.49229	2.56809	0.18128
O	1.10155	-0.57283	0.53856
O	-2.42619	-0.85583	-0.51779
O	-1.64312	1.61642	0.23527
O	0.61317	2.83684	-0.73524
O	2.58551	1.17551	0.49873
O	0.51486	-3.10521	-0.44044

Structure 3: B3LYP/6-311++G(d,p)-optimized geometry of altrose, α-tg-(g-), 'crcc'

24
Energy: -687.0541519

C	1.27407	-1.26795	0.77427
C	-0.12478	-1.50998	1.36499
C	-1.20837	-0.99044	0.40364
C	-0.94149	0.46247	-0.00991
C	0.51974	0.65605	-0.45898
C	0.88961	2.12756	-0.64024
H	2.04294	-1.47925	1.51833
H	-0.27429	-2.58045	1.52136
H	-2.18500	-1.05062	0.89563
H	-1.13461	1.10886	0.85784
H	0.67502	0.12575	-1.40691
H	1.94687	2.21119	-0.90573
H	0.72981	2.66793	0.29567
H	0.22794	-0.04358	2.59999
H	-1.70862	-1.39086	-1.43498
H	-1.60785	1.60404	-1.44317
H	0.45320	2.65868	-2.49244
H	0.70516	-2.20069	-0.82259
O	-0.23847	-0.88792	2.63872
O	-1.19268	-1.84251	-0.75185
O	-1.86678	0.75412	-1.05549
O	1.41529	0.14621	0.53285
O	0.05207	2.76063	-1.62351
O	1.54160	-2.03990	-0.35475

Structure 4: B3LYP/6-311++G(d,p)-optimized geometry of altrose, β-tg-(t), 'cOcc'

24
Energy: -687.0516986

C	1.27542	-1.32555	0.48026

C	-0.07145	-1.60318	1.16149
C	-1.23246	-1.05030	0.32390
C	-0.99856	0.41297	-0.09293
C	0.42321	0.59476	-0.66005
C	0.80367	2.05221	-0.89708
H	1.34373	-1.82990	-0.48761
H	-0.20690	-2.67994	1.27721
H	-2.15559	-1.10597	0.91450
H	-1.10558	1.05911	0.79258
H	0.49902	0.04153	-1.60622
H	1.81191	2.09629	-1.32062
H	0.80092	2.58820	0.05991
H	0.12895	-0.11925	2.42497
H	-1.90757	-1.41232	-1.45022
H	-1.76108	1.52973	-1.49955
H	0.04215	3.54689	-1.94756
H	2.12524	-1.56008	2.17707
O	-0.04839	-1.06656	2.48661
O	-1.32839	-1.87658	-0.83022
O	-2.01491	0.71326	-1.04368
O	1.38016	0.10095	0.27823
O	-0.15929	2.61807	-1.80026
O	2.34709	-1.73782	1.25186

Structure 5: B3LYP/6-311++G(d,p)-optimized geometry of galactose, α-gg-(g+), 'cccc'

24
Energy: -687.0569897

C	-0.44524	-1.54878	0.67829
C	0.90259	-0.92902	1.07234
C	0.83708	0.60093	1.07741
C	0.29459	1.11855	-0.25607
C	-1.03292	0.41175	-0.57856
C	-1.59101	0.73531	-1.96042
H	-0.33219	-2.62242	0.49615
H	1.65223	-1.25271	0.34137
H	0.17615	0.92400	1.88592
H	0.09059	2.19567	-0.16496
H	-1.77006	0.72889	0.17024
H	-1.70311	1.81547	-2.07508
H	-2.57552	0.26980	-2.07054
H	1.96890	-0.90895	2.70013
H	2.62448	1.14024	0.55078
H	0.92340	0.81606	-2.09472
H	-0.98006	-1.43453	2.52993
H	-0.67878	-0.65701	-2.97623

O	1.22260	-1.42645	2.37164
O	2.12098	1.14375	1.37727
O	1.32832	0.90838	-1.21770
O	-0.90216	-1.01798	-0.54121
O	-0.71569	0.30709	-3.01151
O	-1.42213	-1.31976	1.67665

Structure 6: B3LYP/6-311++G(d,p)-optimized geometry of galactose, β-gt-(g-), 'rrrr'

24
Energy: -687.0534685

C	-0.36397	-0.91276	-0.80045
C	1.23151	-0.38220	0.89828
C	0.51451	0.92330	1.23474
C	-0.97595	0.77764	0.94837
C	-1.21667	0.32484	-0.49656
C	-0.38870	-1.32329	-2.26765
H	-0.75139	-1.74704	-0.19507
H	-1.38802	0.02105	1.63169
H	-1.36603	2.39174	1.96575
H	0.01921	-0.50988	-2.87466
H	1.23185	-2.38574	-2.21336
H	-1.42014	-1.50399	-2.57761
H	-2.27475	0.04055	-0.59626
H	-1.28533	2.17416	-1.05656
H	0.94016	1.70514	0.59544
H	1.57180	1.40260	2.80669
H	0.85530	-1.20213	1.53368
H	3.06831	-1.00477	0.98330
O	1.02027	-0.70726	-0.46589
O	2.59708	-0.17388	1.11138
O	0.63692	1.26890	2.61249
O	-1.66282	2.01313	1.12895
O	-0.90310	1.36166	-1.41374
O	0.31872	-2.53864	-2.48153

Structure 7: B3LYP/6-311++G(d,p)-optimized geometry of glucose, α-gt-(g-), 'rrrr'

24
Energy: -687.0560768

C	-0.85380	0.70940	-0.39363
C	0.64096	1.02924	-0.30996
C	1.30857	0.09847	0.69689
C	1.03882	-1.36740	0.34779
C	-0.46536	-1.61307	0.16719

C	-1.57242	1.49634	-1.47968
H	-1.32657	0.91079	0.57340
H	1.10049	0.86422	-1.29604
H	0.90035	0.31820	1.69279
H	1.54132	-1.59888	-0.59478
H	-0.64598	-2.59332	-0.28262
H	-1.09139	1.29764	-2.44761
H	-1.48688	2.56122	-1.26386
H	1.71308	2.54362	0.26117
H	3.14596	-0.25102	1.25508
H	0.99404	-2.26257	2.07028
H	-1.94615	-1.86084	1.42969
H	-3.03755	0.24338	-1.68528
O	-1.03306	-0.68709	-0.72975
O	0.77889	2.39159	0.07276
O	2.70626	0.38346	0.67606
O	1.60428	-2.23964	1.32045
O	-1.03589	-1.54649	1.46483
O	-2.95960	1.19133	-1.52897

Structure 8: B3LYP/6-311++G(d,p)-optimized geometry of glucose, β-gg-(g+), 'rrrr'

24
Energy: -687.0545109

C	-1.05249	0.61764	-0.41075
C	0.39830	1.11549	-0.36448
C	1.14668	0.48583	0.80712
C	1.01008	-1.03058	0.79194
C	-0.46980	-1.40734	0.74142
C	-1.79640	1.04079	-1.67352
H	-1.58859	1.01318	0.46514
H	0.90013	0.83771	-1.29939
H	0.71116	0.86414	1.74403
H	1.48950	-1.43981	-0.10665
H	-0.98393	-1.05813	1.65209
H	-2.84811	0.74107	-1.57657
H	-1.74848	2.12582	-1.76987
H	1.26044	2.84355	-0.14330
H	2.99316	0.48210	1.43358
H	1.60565	-2.48360	1.95456
H	-1.20494	-0.46500	-2.74416
H	-1.47134	-3.06589	0.66703
O	-1.08531	-0.82065	-0.39707
O	-0.54645	-2.79757	0.62580
O	0.35182	2.53209	-0.23207
O	2.50679	0.89879	0.71227

O	1.64429	-1.52044	1.96989
O	-1.21922	0.49365	-2.85034

Structure 9: B3LYP/6-311++G(d,p)-optimized geometry of gulose, α-gg-(g+), 'rcrc'

24
Energy: -687.0537183

C	0.10610	1.56463	0.49002
C	-1.35388	1.09395	0.36762
C	-1.45891	-0.41910	0.60395
C	-0.49256	-1.15500	-0.34514
C	0.92934	-0.58711	-0.21857
C	1.93225	-1.13870	-1.22611
H	0.19957	2.61102	0.19096
H	-1.66079	1.29376	-0.66041
H	-2.47281	-0.74476	0.36427
H	-0.45589	-2.21087	-0.03930
H	1.30186	-0.84221	0.78258
H	1.96247	-2.22823	-1.15853
H	2.93022	-0.75102	-0.99367
H	-2.14052	1.48398	2.09874
H	-0.46428	-0.30145	2.29422
H	-0.33666	-1.12626	-2.29827
H	1.34776	1.84959	1.98951
H	1.60283	0.13197	-2.66786
O	-2.21397	1.84158	1.20486
O	-1.25230	-0.76283	1.97419
O	-1.04898	-1.03005	-1.64832
O	0.95857	0.84690	-0.38467
O	0.50647	1.40156	1.84778
O	1.58347	-0.82912	-2.57926

Structure 10: B3LYP/6-311++G(d,p)-optimized geometry of gulose, β-gg-(g+), 'rrrc'

24
Energy: -687.0538099

C	0.18037	1.38620	0.76756
C	-1.27143	0.91746	0.60660
C	-1.37552	-0.60989	0.65687
C	-0.40894	-1.23373	-0.35533
C	1.00471	-0.66686	-0.13944
C	2.04215	-1.14624	-1.14740
H	0.54576	1.15890	1.77521
H	-1.63881	1.25847	-0.36986
H	-2.39800	-0.90628	0.39494
H	-0.36845	-2.31554	-0.16354

H	1.33015	-0.98549	0.86063
H	2.07741	-2.23768	-1.15051
H	3.02917	-0.76952	-0.85921
H	-1.91109	2.36986	1.75128
H	-1.53108	-0.58864	2.59034
H	-0.21629	-1.00816	-2.28544
H	1.79997	0.21013	-2.53008
H	0.12112	2.99778	-0.29763
O	0.29001	2.77670	0.62793
O	-2.08272	1.42451	1.66459
O	-1.02226	-1.09854	1.94728
O	-0.94333	-0.96931	-1.64561
O	1.00956	0.76989	-0.20885
O	1.73184	-0.75148	-2.48980

Structure 11: B3LYP/6-311++G(d,p)-optimized geometry of idose, α-gg-(g+), 'cccc'

24
Energy: -687.0539136

C	1.38380	-0.91537	0.74676
C	0.01080	-1.56185	1.03426
C	-0.97696	-1.28466	-0.11527
C	-1.02985	0.22039	-0.44225
C	0.39143	0.76405	-0.66494
C	0.45838	2.27383	-0.86768
H	1.99092	-0.93019	1.65089
H	1.48894	2.55813	-1.10267
H	0.15858	-2.64161	1.11477
H	-1.97282	-1.61826	0.19383
H	-1.60409	0.36827	-1.37098
H	0.79218	0.28829	-1.57052
H	-0.18341	2.57453	-1.69888
H	-0.95153	-0.26981	2.11883
H	-1.18582	-2.02886	-1.94339
H	-1.43368	1.77468	0.68251
H	1.47540	-1.93886	-0.90892
H	0.61249	2.81496	0.99925
O	-0.51443	-1.12181	2.27261
O	-0.51714	-2.03731	-1.25051
O	-1.71035	0.84236	0.65000
O	1.23162	0.47841	0.45299
O	2.09821	-1.58984	-0.25536
O	-0.00802	2.99442	0.28120

Structure 12: B3LYP/6-311++G(d,p)-optimized geometry of idose, β-gg-(g+), 'cccc'

24
Energy: -687.0555358

C	1.44762	-0.76013	0.70067
C	0.16292	-1.59588	0.86397
C	-0.77021	-1.44792	-0.34699
C	-1.00894	0.03807	-0.66930
C	0.34084	0.76165	-0.80179
C	0.22106	2.26427	-1.03515
H	1.21586	2.68508	-1.21294
H	2.07700	-1.16378	-0.09983
H	0.45243	-2.64516	0.95733
H	-1.72828	-1.92100	-0.10531
H	-1.54369	0.11565	-1.62838
H	0.86615	0.32060	-1.66232
H	-0.40210	2.46591	-1.90938
H	-1.05826	-0.47037	1.88208
H	-0.79389	-2.30245	-2.11979
H	-1.68147	1.52079	0.42352
H	0.18459	2.83082	0.82766
H	1.55152	-0.70328	2.59647
O	2.18908	-0.75922	1.86762
O	-0.49060	-1.23493	2.07743
O	-0.13483	-2.10465	-1.44703
O	-1.82262	0.55886	0.38684
O	1.11906	0.60790	0.38387
O	-0.40668	2.92892	0.07003

Structure 13: B3LYP/6-311++G(d,p)-optimized geometry of mannose, α-gg-(g+), 'rccc'

24
Energy: -687.0546874

C	-0.39689	-1.52887	0.99869
C	1.07131	-1.09564	1.05364
C	1.20593	0.41522	0.84333
C	0.44235	0.85322	-0.40114
C	-1.02894	0.42883	-0.27479
C	-1.87144	0.74715	-1.50253
H	-0.44614	-2.61202	0.85984
H	-1.91345	1.82821	-1.65075
H	1.46610	-1.35717	2.04241
H	0.79023	0.93598	1.71533
H	0.87861	0.37220	-1.28034
H	-1.47337	0.92575	0.59726
H	-2.89420	0.39111	-1.32575
H	2.62480	-1.40322	-0.05567
H	2.68953	1.61131	0.45411

H	0.50430	2.53632	-1.41828
H	-1.89288	-1.46970	2.23673
H	-1.25337	-0.76099	-2.56042
O	1.75648	-1.81619	0.03821
O	2.60101	0.68940	0.72513
O	0.58246	2.27737	-0.49469
O	-1.09417	-1.00172	-0.11573
O	-0.98990	-1.13312	2.21953
O	-1.33634	0.19078	-2.69678

Structure 14: B3LYP/6-311++G(d,p)-optimized geometry of mannose, β-gg-(g+), 'cccc'

24
Energy: -687.0542718

C	-0.57090	-1.43598	1.05864
C	0.91247	-1.04339	1.17086
C	1.10853	0.45827	0.96360
C	0.40041	0.93491	-0.29915
C	-1.08080	0.52749	-0.23282
C	-1.88156	0.91372	-1.47096
H	-1.89933	2.00061	-1.57814
H	-1.12218	-1.05956	1.93050
H	1.26025	-1.31794	2.17548
H	0.67650	0.99371	1.82238
H	0.85436	0.45998	-1.17288
H	-1.54939	1.00374	0.64421
H	-2.91420	0.56927	-1.33776
H	2.51434	-1.44947	0.14609
H	2.63959	1.60624	0.62400
H	0.50610	2.64103	-1.27181
H	-1.28985	-0.56620	-2.58170
H	-0.06265	-3.16675	0.43431
O	-0.73136	-2.81039	1.03689
O	1.61585	-1.79979	0.19189
O	2.51311	0.69171	0.90589
O	0.58004	2.35576	-0.35555
O	-1.16215	-0.89531	-0.12804
O	-1.31782	0.39449	-2.66863

Structure 15: B3LYP/6-311++G(d,p)-optimized geometry of talose, α-gg-(g+), 'rcrc'

24
Energy: -687.0570870

C	0.10101	1.51292	0.94377
C	-1.27198	0.82415	1.03429
C	-1.10567	-0.70696	1.01587

C	-0.27183	-1.13242	-0.20304
C	1.07539	-0.39099	-0.17043
C	1.98421	-0.67368	-1.36153
H	-0.03742	2.57545	0.72922
H	2.16791	-1.74730	-1.44042
H	-1.73678	1.12373	1.97555
H	-0.55551	-1.00059	1.91381
H	-0.08273	-2.21294	-0.14656
H	1.60557	-0.70747	0.73831
H	2.94474	-0.16847	-1.21279
H	-1.85947	0.83197	-0.81809
H	-2.91855	-1.01088	0.39259
H	-0.42463	-0.81092	-2.13527
H	1.54810	1.86104	2.19894
H	1.31182	0.68694	-2.58710
O	-2.13392	1.27768	-0.00014
O	-2.34917	-1.37672	1.08120
O	-1.03560	-0.83755	-1.38116
O	0.88241	1.03317	-0.14590
O	0.75784	1.30974	2.17782
O	1.40017	-0.27416	-2.60737

Structure 16: B3LYP/6-311++G(d,p)-optimized geometry of talose, β-gg-(g+), 'ccrc'

24
Energy: -687.0578393

C	0.37710	1.40276	1.07960
C	-1.08633	0.91752	1.09119
C	-1.16292	-0.61694	1.04879
C	-0.34216	-1.15578	-0.13150
C	1.09308	-0.60708	-0.03317
C	2.00482	-1.02905	-1.18268
H	3.01982	-0.66593	-0.99167
H	0.88826	1.12716	2.01195
H	-1.55907	1.27925	2.00797
H	-0.71514	-1.00542	1.97000
H	-0.31605	-2.25239	-0.08049
H	1.53604	-0.99522	0.90005
H	-1.57858	1.02139	-0.78977
H	-2.95867	-0.67966	0.30845
H	-0.36254	-0.79422	-2.06275
H	2.03394	-2.11824	-1.25776
H	-0.26102	3.03554	0.34443
H	1.60672	0.41208	-2.43330
O	0.44601	2.77711	0.95612
O	-1.79960	1.52478	0.01334

O	-2.49529	-1.09067	1.04886
O	-1.00448	-0.74248	-1.33498
O	1.09638	0.81865	-0.02329
O	1.53530	-0.55079	-2.44878

Structure 17: B3LYP-PCM/6-311++G(d,p)-optimized geometry of allose, α-tg-(g-), 'cOcc'

24
Energy: -687.0546749

C	-0.60667	-0.48972	-0.78694
C	-0.36063	0.98753	-1.09347
C	1.11745	1.33150	-0.93032
C	1.62304	0.90313	0.46152
C	-0.00996	-0.86733	0.57931
C	-0.04366	-2.37121	0.84330
H	1.68599	0.76666	-1.67010
H	-0.57662	-0.35466	1.36566
H	-0.12503	-1.09409	-1.56658
H	-0.68175	1.21171	-2.11494
H	2.70567	0.99925	0.51892
H	0.39750	-2.58259	1.81791
H	0.52756	-2.89466	0.07502
H	0.86759	3.22994	-0.57155
H	-1.99890	1.46085	-0.14407
H	-2.20071	-1.53044	-0.38464
H	-1.77927	-2.84092	1.65297
H	0.15166	1.85451	1.30404
O	1.37022	-0.48873	0.64269
O	-2.02141	-0.67487	-0.81018
O	-1.09811	1.81329	-0.17361
O	1.38130	2.70098	-1.19461
O	-1.39031	-2.86960	0.77239
O	1.09240	1.69632	1.49391

Structure 18: B3LYP-PCM/6-311++G(d,p)-optimized geometry of allose, β-gt-(g-), 'rrrr'

24
Energy: -687.0525526

C	-0.36734	0.95655	-0.55880
C	1.49500	-0.36711	0.10078
C	0.65168	-1.22576	1.03934
C	-0.79901	-1.27247	0.56777
C	-1.35002	0.12988	0.28904
C	-0.77613	2.41396	-0.65234
H	-0.29868	0.52501	-1.56561
H	1.51056	-0.79161	-0.91035

H	3.39837	-0.01356	-0.04305
H	0.69566	-0.76430	2.03300
H	2.07132	-2.54557	1.23849
H	-1.41235	-1.75571	1.33530
H	-0.40763	-2.82076	-0.55586
H	-1.50784	0.64327	1.24085
H	-2.56041	-0.67612	-0.99096
H	-0.78462	2.84357	0.35654
H	0.98665	3.04441	-1.17191
H	-1.77853	2.48302	-1.07249
O	0.93652	0.94224	0.05001
O	2.78045	-0.29748	0.64000
O	1.11946	-2.56990	1.07924
O	-0.90971	-2.00197	-0.65864
O	-2.62141	0.04128	-0.34485
O	0.08880	3.15817	-1.50618

Structure 19: B3LYP-PCM/6-311++G(d,p)-optimized geometry of altrose, α-tg-(t), 'crcc'

24
Energy: -687.0532664

C	1.28320	-1.31637	0.73078
C	-0.11382	-1.55404	1.32307
C	-1.19415	-1.02419	0.36877
C	-0.92197	0.42988	-0.02599
C	0.53341	0.61837	-0.49237
C	0.91213	2.08367	-0.65645
H	2.04604	-1.53908	1.47454
H	-0.26346	-2.62317	1.47548
H	-2.17285	-1.08987	0.85340
H	-1.09565	1.06687	0.85070
H	0.67295	0.10352	-1.44866
H	1.95354	2.15468	-0.97873
H	0.79531	2.60181	0.29978
H	0.19241	-0.06436	2.54914
H	-1.62689	-1.36936	-1.49776
H	-1.53552	1.55982	-1.48367
H	0.09887	3.60373	-1.62212
H	0.69922	-2.22571	-0.87801
O	-0.21511	-0.93871	2.60181
O	-1.17264	-1.86220	-0.79809
O	-1.85192	0.74323	-1.06131
O	1.44156	0.08747	0.48290
O	0.03325	2.64355	-1.64457

O	1.53846	-2.09822	-0.40120

Structure 20: B3LYP-PCM/6-311++G(d,p)-optimized geometry of altrose, β-tg-(t), 'cccc'

24
Energy: -687.0512083

C	1.31494	-1.26248	0.45423
C	-0.04117	-1.57755	1.09964
C	-1.20321	-0.98351	0.29927
C	-0.94421	0.47773	-0.08209
C	0.45450	0.64339	-0.69871
C	0.82568	2.09868	-0.95037
H	1.41937	-1.80373	-0.49013
H	-0.15832	-2.66418	1.13447
H	-2.11669	-1.02996	0.90444
H	-1.00073	1.09345	0.82355
H	0.49722	0.08931	-1.64599
H	1.83675	2.15063	-1.35965
H	0.79150	2.65089	-0.00685
H	-0.59731	-1.52144	2.98551
H	-1.89281	-1.25485	-1.48367
H	-1.68208	1.62883	-1.47364
H	0.01923	3.57956	-1.97516
H	2.09555	-1.39669	2.18456
O	0.01257	-1.03480	2.42191
O	-1.35380	-1.77975	-0.87455
O	-1.97980	0.83346	-1.00099
O	1.43912	0.14252	0.20678
O	-0.12861	2.63331	-1.88094
O	2.36197	-1.64190	1.28518

Structure 21: B3LYP-PCM/6-311++G(d,p)-optimized geometry of galactose, α-gg-(g-), 'rrrr'

24
Energy: -687.0542811

C	-1.07499	0.60548	0.30746
C	-0.44908	-1.14477	-1.21798
C	1.00454	-1.10437	-0.73544
C	1.07563	-0.61690	0.71068
C	0.34572	0.71563	0.86624
C	-1.84447	1.92260	0.32172
H	-1.61946	-0.09543	0.95145
H	-0.49258	-1.33960	-2.29027
H	-1.89278	-2.43922	-0.95083
H	0.59551	-1.35421	1.36388
H	2.94948	-1.15461	0.78970

H	-1.88103	2.27236	1.36072
H	-0.35162	2.93005	-0.40455
H	-2.86417	1.73591	-0.01514
H	0.27864	0.96367	1.93215
H	1.98751	1.66677	0.40297
H	1.55853	-0.41358	-1.37085
H	1.01872	-3.03526	-0.54041
O	-1.08234	0.10293	-1.04069
O	-1.07979	-2.18990	-0.49747
O	1.63846	-2.37238	-0.87615
O	2.42845	-0.40938	1.11529
O	1.05121	1.75660	0.17977
O	-1.31220	2.92964	-0.53308

Structure 22: B3LYP-PCM/6-311++G(d,p)-optimized geometry of galactose, β-gg-(g-), 'rrrr'

24
Energy: -687.0526425

C	-0.26881	-1.03869	-0.78373
C	1.26938	-0.52814	0.96562
C	0.55370	0.78084	1.28977
C	-0.92415	0.66116	0.94468
C	-1.11627	0.20882	-0.50203
C	-0.31064	-1.49577	-2.23894
H	-0.69428	-1.85382	-0.17979
H	-1.37580	-0.08734	1.60770
H	-1.31882	2.28776	1.94087
H	-1.35732	-1.69919	-2.49730
H	-0.04720	0.30155	-2.92263
H	0.24902	-2.42714	-2.32722
H	-2.17099	-0.04807	-0.65430
H	-1.13990	2.07255	-1.08185
H	1.01304	1.57068	0.68586
H	1.54886	1.30137	2.88432
H	0.86695	-1.34997	1.57524
H	3.06356	-1.19775	1.26287
O	1.10090	-0.83880	-0.41391
O	2.62817	-0.33913	1.21926
O	0.62845	1.10483	2.67494
O	-1.59458	1.91061	1.09585
O	-0.74385	1.25298	-1.40705
O	0.27433	-0.58142	-3.15918

Structure 23: B3LYP-PCM/6-311++G(d,p)-optimized geometry of glucose, α-tg-(g+), 'rrrr'

24

Energy: -687.0533324

C	-0.94888	0.54265	-0.47421
C	0.54640	0.85938	-0.36140
C	1.19020	-0.02979	0.69074
C	0.91594	-1.50289	0.38105
C	-0.58454	-1.74341	0.17346
C	-1.64169	1.32379	-1.58896
H	-1.43756	0.76825	0.47942
H	1.02744	0.67123	-1.32997
H	0.76447	0.22298	1.66945
H	1.43776	-1.77114	-0.53916
H	-0.76306	-2.73763	-0.23686
H	-2.65991	0.95062	-1.70057
H	-1.11044	1.15683	-2.53366
H	1.61650	2.44212	0.07841
H	3.00285	-0.33157	1.34101
H	0.82273	-2.31484	2.14063
H	-2.05680	-2.03497	1.42857
H	-0.86302	2.99924	-0.98423
O	-1.11475	-0.84908	-0.78727
O	0.67707	2.24420	-0.02257
O	2.58929	0.24832	0.69007
O	1.44360	-2.34637	1.39919
O	-1.19371	-1.60602	1.44133
O	-1.73717	2.71334	-1.29002

Structure 24: B3LYP-PCM/6-311++G(d,p)-optimized geometry of glucose, β-gg-(g+), 'rrrr'

24

Energy: -687.0517072

C	-1.04757	0.60383	-0.41745
C	0.40564	1.08880	-0.38565
C	1.13943	0.47409	0.79902
C	0.99545	-1.03996	0.79882
C	-0.48212	-1.42328	0.71973
C	-1.81022	1.06636	-1.64923
H	-1.56897	0.97357	0.47600
H	0.89901	0.77568	-1.31276
H	0.70094	0.86424	1.72714
H	1.49442	-1.46208	-0.08184
H	-1.02250	-1.07631	1.61131
H	-2.84227	0.71153	-1.57490
H	-1.80334	2.15411	-1.68496
H	1.30631	2.79199	-0.14973
H	2.96723	0.50972	1.47398
H	1.56742	-2.48569	1.97443

H	-1.18560	-0.35481	-2.81718
H	-1.43466	-3.10971	0.83376
O	-1.07055	-0.83233	-0.43839
O	-0.54892	-2.81019	0.60005
O	0.39439	2.51070	-0.29390
O	2.50439	0.87988	0.71298
O	1.60028	-1.52207	1.99412
O	-1.20866	0.60863	-2.85820

Structure 25: B3LYP-PCM/6-311++G(d,p)-optimized geometry of gulose, α-gg-(g+), 'rcrc'

24
Energy: -687.0533920

C	0.08838	1.56288	0.49867
C	-1.36651	1.08709	0.37139
C	-1.46556	-0.42699	0.59874
C	-0.49414	-1.15122	-0.34877
C	0.92182	-0.57585	-0.21892
C	1.92336	-1.13798	-1.21663
H	0.18256	2.61148	0.21510
H	-1.68157	1.29506	-0.65057
H	-2.47787	-0.75532	0.35935
H	-0.45286	-2.20812	-0.05585
H	1.29394	-0.82214	0.78244
H	1.97590	-2.22099	-1.10583
H	2.91029	-0.71416	-1.02146
H	-2.05257	1.54759	2.13008
H	-0.46444	-0.31763	2.28811
H	-0.29703	-1.04213	-2.28920
H	1.30280	1.83671	2.02534
H	1.68285	0.04927	-2.75769
O	-2.23249	1.82165	1.22183
O	-1.25282	-0.78070	1.96620
O	-1.03944	-1.02271	-1.66167
O	0.93300	0.85644	-0.39149
O	0.47365	1.37538	1.85302
O	1.54383	-0.88886	-2.58063

Structure 26: B3LYP-PCM/6-311++G(d,p)-optimized geometry of gulose, β-gg-(g+), 'Orrc'

24
Energy: -687.0514990

C	0.19626	1.37761	0.78142
C	-1.25744	0.92765	0.60967
C	-1.37614	-0.59728	0.64746
C	-0.40274	-1.23261	-0.34784

C	1.00990	-0.66182	-0.14464
C	2.03835	-1.15040	-1.15402
H	0.56367	1.11311	1.77812
H	-1.61222	1.28294	-0.36504
H	-2.39817	-0.87715	0.36931
H	-0.35911	-2.30932	-0.14103
H	1.34425	-0.97293	0.85348
H	2.10599	-2.23747	-1.10932
H	3.01269	-0.72350	-0.90992
H	-1.89390	2.37521	1.76073
H	-1.52227	-0.53369	2.58025
H	-0.17444	-0.99131	-2.26604
H	1.81370	0.13039	-2.61831
H	0.04096	3.03734	-0.20357
O	0.32007	2.76743	0.68201
O	-2.07064	1.43109	1.66729
O	-1.05952	-1.09586	1.94493
O	-0.92763	-0.99455	-1.65155
O	1.00843	0.77490	-0.21778
O	1.68310	-0.81893	-2.50774

Structure 27: B3LYP-PCM/6-311++G(d,p)-optimized geometry of idose *α*-gg-(g+), 'cccc'

24
Energy: -687.0548006

C	1.37659	-0.93117	0.74465
C	0.00442	-1.57198	1.03924
C	-0.97946	-1.29928	-0.10986
C	-1.03295	0.20588	-0.42537
C	0.38161	0.74845	-0.66655
C	0.44371	2.25356	-0.87857
H	1.98827	-0.95527	1.64408
H	1.47457	2.54185	-1.09308
H	0.15000	-2.64936	1.13050
H	-1.97692	-1.63767	0.18395
H	-1.62303	0.36603	-1.33701
H	0.76941	0.27131	-1.57430
H	-0.18551	2.53730	-1.72198
H	-0.95349	-0.26100	2.10183
H	-1.09148	-1.92674	-1.98586
H	-1.39064	1.75462	0.71958
H	1.43916	-1.91397	-0.93399
H	0.58702	2.87668	0.97195
O	-0.51338	-1.11035	2.27773
O	-0.49781	-2.04437	-1.23506
O	-1.68475	0.82563	0.69277

O	1.24089	0.45707	0.44512
O	2.07698	-1.62233	-0.26273
O	-0.05134	2.98378	0.25619

Structure 28: B3LYP-PCM/6-311++G(d,p)-optimized geometry of idose β-gg-(g+), 'cccc'

24
Energy: -687.0550078

C	1.44191	-0.77758	0.69038
C	0.16086	-1.61264	0.86211
C	-0.77563	-1.46395	-0.34238
C	-1.01115	0.02225	-0.65506
C	0.33325	0.74546	-0.80488
C	0.20515	2.24236	-1.04815
H	1.19475	2.67625	-1.20769
H	2.06848	-1.18966	-0.10590
H	0.45188	-2.66000	0.95793
H	-1.73459	-1.93298	-0.10256
H	-1.56514	0.11025	-1.59841
H	0.84967	0.30485	-1.66760
H	-0.40501	2.42113	-1.93347
H	-1.04065	-0.46632	1.87406
H	-0.76450	-2.17910	-2.17069
H	-1.64040	1.50530	0.45841
H	0.14081	2.88792	0.79769
H	1.53772	-0.72680	2.59000
O	2.18244	-0.77880	1.86655
O	-0.48664	-1.24128	2.07858
O	-0.14257	-2.12393	-1.43660
O	-1.79875	0.54417	0.42645
O	1.12734	0.58785	0.37800
O	-0.45638	2.91061	0.03970

Structure 29: B3LYP-PCM/6-311++G(d,p)-optimized geometry of mannose, α-tg-(g+), 'rrrr'

24
Energy: -687.0519085

C	-0.89791	-1.30901	1.00284
C	0.60898	-1.17059	1.27241
C	1.10016	0.23500	0.92240
C	0.63334	0.61964	-0.48031
C	-0.88946	0.49768	-0.58616
C	-1.42043	0.79592	-1.98688
H	-1.18279	-2.36351	1.00414
H	-2.48460	0.56125	-2.01627
H	0.79320	-1.37323	2.32978

H	0.69184	0.95012	1.63901
H	1.08942	-0.05845	-1.21208
H	-1.35953	1.18147	0.12930
H	-0.90344	0.15784	-2.71305
H	1.37608	-2.93984	0.86485
H	2.87416	-0.49386	0.65250
H	1.94624	2.05818	-0.63667
H	-2.50590	-0.77938	1.95224
H	-0.38573	2.43799	-2.08779
O	1.35899	-2.06974	0.45295
O	2.51921	0.32803	1.02161
O	0.99616	1.97051	-0.78517
O	-1.26363	-0.85615	-0.28871
O	-1.56157	-0.59616	2.02264
O	-1.28600	2.17281	-2.33049

Structure 30: B3LYP-PCM/6-311++G(d,p)-optimized geometry of mannose, β-tg-(t), 'cccc'

24
Energy: -687.0520000

C	-0.70678	-1.42651	1.12295
C	0.80232	-1.18337	1.25424
C	1.13840	0.27616	0.97870
C	0.52652	0.76186	-0.32789
C	-0.98156	0.46224	-0.33443
C	-1.64749	0.77279	-1.66963
H	-1.24112	-0.93154	1.94069
H	1.10040	-1.43624	2.27780
H	0.72166	0.88730	1.79028
H	0.99310	0.23127	-1.16723
H	-1.46302	1.04707	0.46228
H	-2.71859	0.57286	-1.59447
H	-1.21354	0.12840	-2.43955
H	2.37839	-1.83743	0.31170
H	2.77161	1.25951	0.59053
H	0.26990	2.52267	-1.11963
H	-1.74649	2.34050	-2.85802
H	-0.34598	-3.24136	0.64653
O	-1.00341	-2.78283	1.19006
O	1.43982	-2.06250	0.33102
O	2.56083	0.39571	0.96712
O	0.81261	2.15792	-0.40188
O	-1.20050	-0.93413	-0.12610
O	-1.40949	2.15426	-1.97606

Structure 31: B3LYP-PCM/6-311++G(d,p)-optimized geometry of talose, *α*-gg-(g+), 'rcrc'

24
Energy: -687.0562701

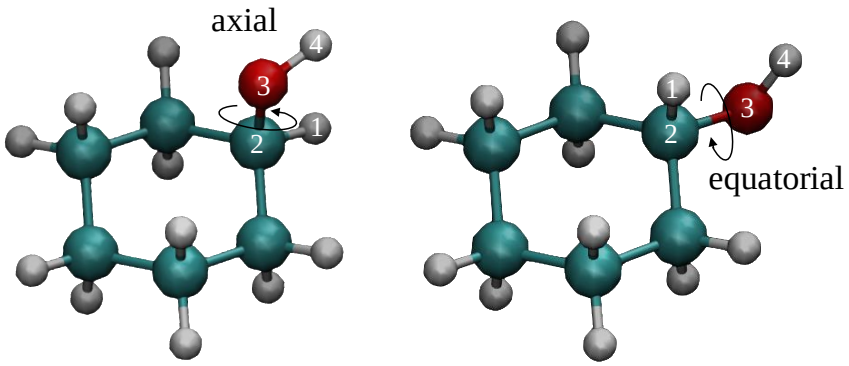
C	0.10393	1.51265	0.95995
C	-1.27057	0.83092	1.04653
C	-1.10633	-0.69784	1.02675
C	-0.27275	-1.12439	-0.18689
C	1.06861	-0.37605	-0.16643
C	1.96781	-0.67559	-1.35588
H	-0.02421	2.58062	0.77704
H	2.16640	-1.74608	-1.39917
H	-1.74157	1.13740	1.98088
H	-0.56822	-0.99999	1.92688
H	-0.07561	-2.20083	-0.13059
H	1.60532	-0.67923	0.74013
H	2.91210	-0.14134	-1.23716
H	-1.83181	0.82478	-0.81209
H	-2.89148	-1.03435	0.33821
H	-0.41504	-0.76673	-2.11010
H	1.54980	1.83008	2.22031
H	1.34353	0.63547	-2.66894
O	-2.12358	1.27883	-0.00291
O	-2.36153	-1.36204	1.07584
O	-1.04243	-0.83617	-1.36842
O	0.86157	1.04716	-0.14940
O	0.76502	1.27109	2.18182
O	1.35631	-0.32755	-2.60982

Structure 32: B3LYP-PCM/6-311++G(d,p)-optimized geometry of talose, β-gg-(g+), 'ccOc'

24
Energy: -687.0574016

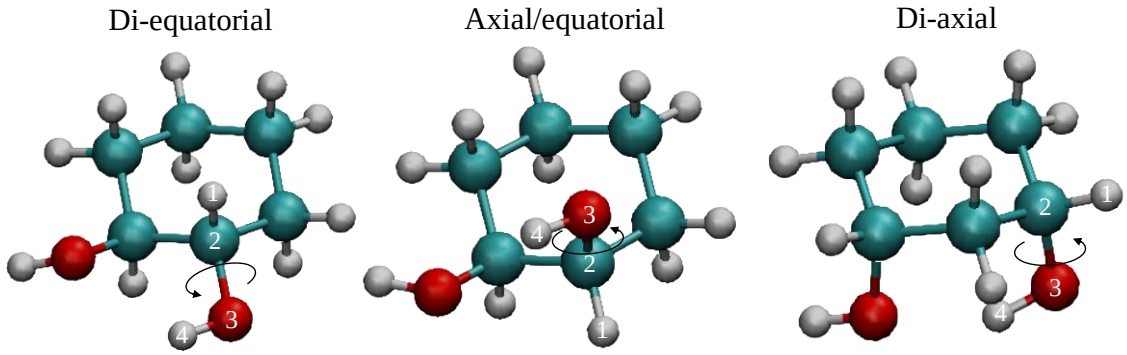
C	0.37364	1.39107	1.09842
C	-1.08977	0.91552	1.10390
C	-1.16515	-0.61606	1.05444
C	-0.34568	-1.14963	-0.12378
C	1.08836	-0.60384	-0.02729
C	1.99176	-1.02857	-1.17758
H	2.99307	-0.62503	-1.01692
H	0.88108	1.10655	2.02720
H	-1.56244	1.27514	2.01895
H	-0.72791	-1.00831	1.97600
H	-0.31533	-2.24362	-0.07888
H	1.53331	-0.98678	0.90247
H	-1.56781	1.02065	-0.78085
H	-2.93709	-0.71704	0.25341
H	-0.35344	-0.75354	-2.04558

H	2.05156	-2.11651	-1.22074
H	-0.26907	3.02997	0.37338
H	1.59841	0.35926	-2.49980
O	0.43886	2.77359	0.98538
O	-1.79079	1.53053	0.01931
O	-2.50565	-1.08363	1.03549
O	-1.01109	-0.72862	-1.32735
O	1.08600	0.82765	-0.01233
O	1.48543	-0.59797	-2.45148



cyclohexanol

Figure S3. The ball and stick representation of cyclohexanol and their indicated direction of rotation. Initial angle is determined by the C-C-O-H dihedral angle (numbered 1, 2, 3, 4) when the hydroxyl and the hydrogen on 2 are eclipsed and set at 0° as reference.



1,2-cyclohexanediol 1,3-cyclohexanediol

Figure S4. The ball and stick representation of 1,2- and 1,3-cyclohexanediol, their indicated direction of rotation, and type of hydrogen bond interaction. Initial angle is determined by the C-C-O-H dihedral angle (numbered 1, 2, 3, 4) from optimized B3LYP geometries and set at 0° as reference.

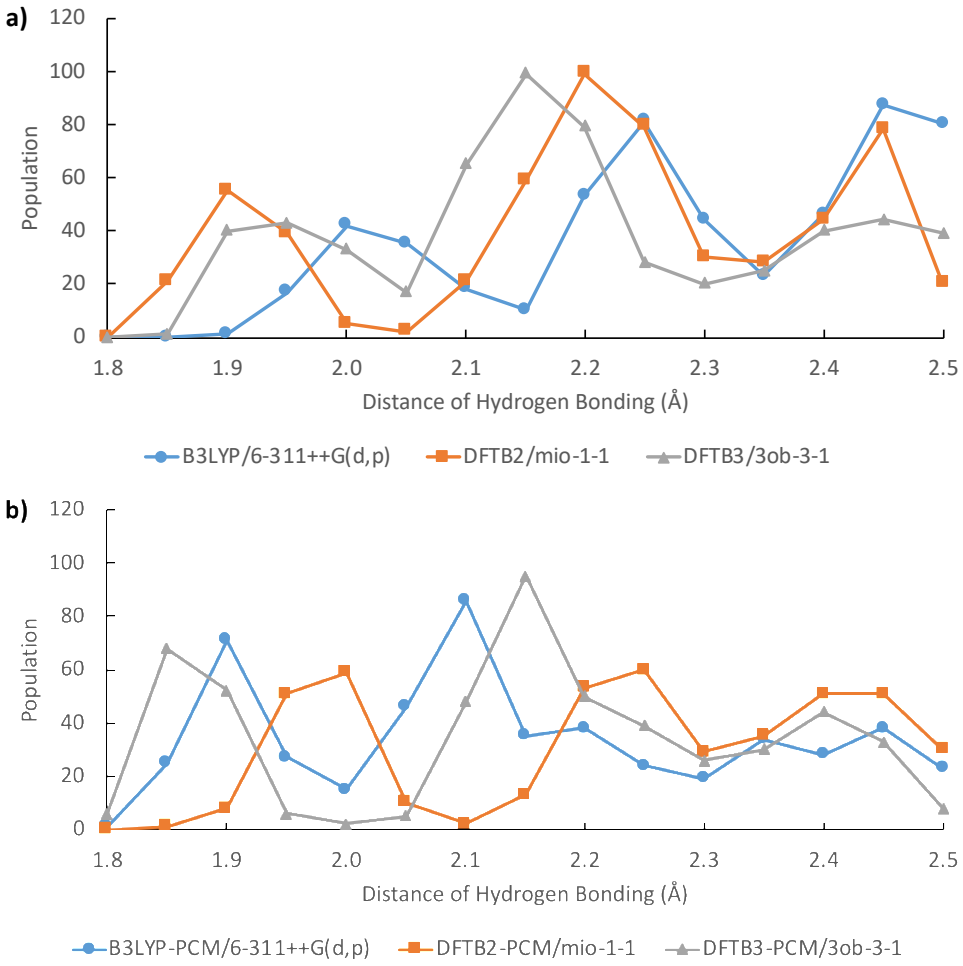


Figure S5. Distribution of hydrogen bonding distances in a) vacuum and in b) implicit solvent.

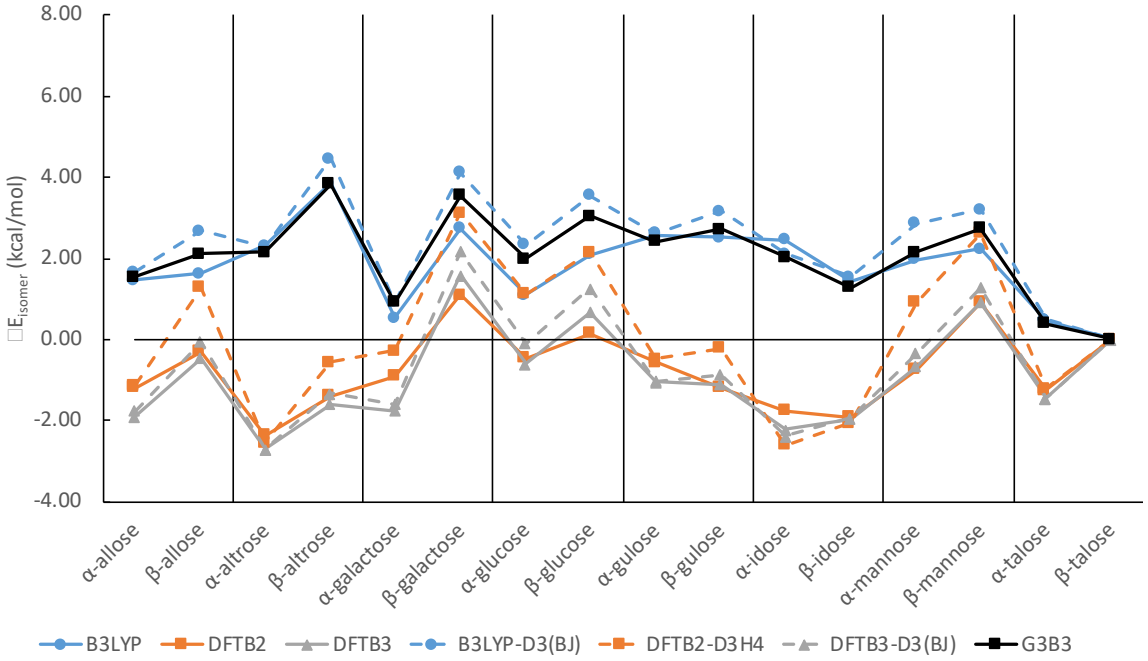


Figure S6. Comparison of ΔE_{isomer} between DFT, DFT-D3, DFTB and DFTB-D3 vs. G3B3 energies from B3LYP/6-311++G(d,p) geometries.

Table S3. The mean absolute deviation, root-mean square deviation, mean signed deviation, and the maximum deviation of $\Delta\Delta E_{isomer}$ (kcal/mol) for B3LYP and B3LYP-D3(BJ) versus G3B3 energies. See explanation of $\Delta\Delta E_{isomer}$ in text from Figure S2.

	Method	
	B3LYP	B3LYP-D3(BJ)
MAD	0.34	0.32
RMSD	0.46	0.39
MSD	-0.22	0.32
MAX	0.95	0.71

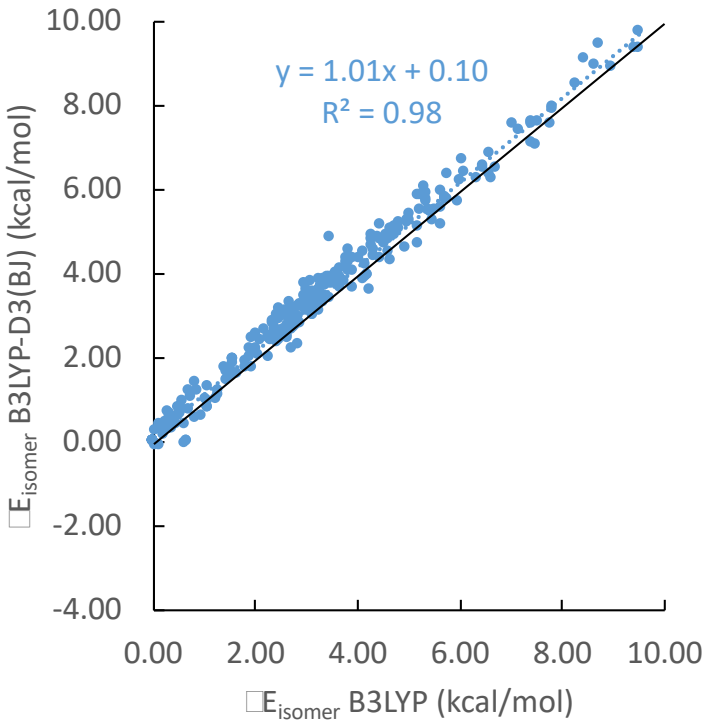


Figure S7. Comparison of δE_{isomer} between B3LYP and B3LYP-D3(BJ) energies from B3LYP/6-311++G(d,p) geometries.

Table S4. The mean absolute deviation, root-mean square deviation, mean signed deviation, and the maximum deviation of δE_{isomer} (kcal/mol) for B3LYP versus B3LYP-D3(BJ) energies.

	Method
	B3LYP
MAD	0.26
RMSD	0.33
MSD	0.15
MAX	1.38

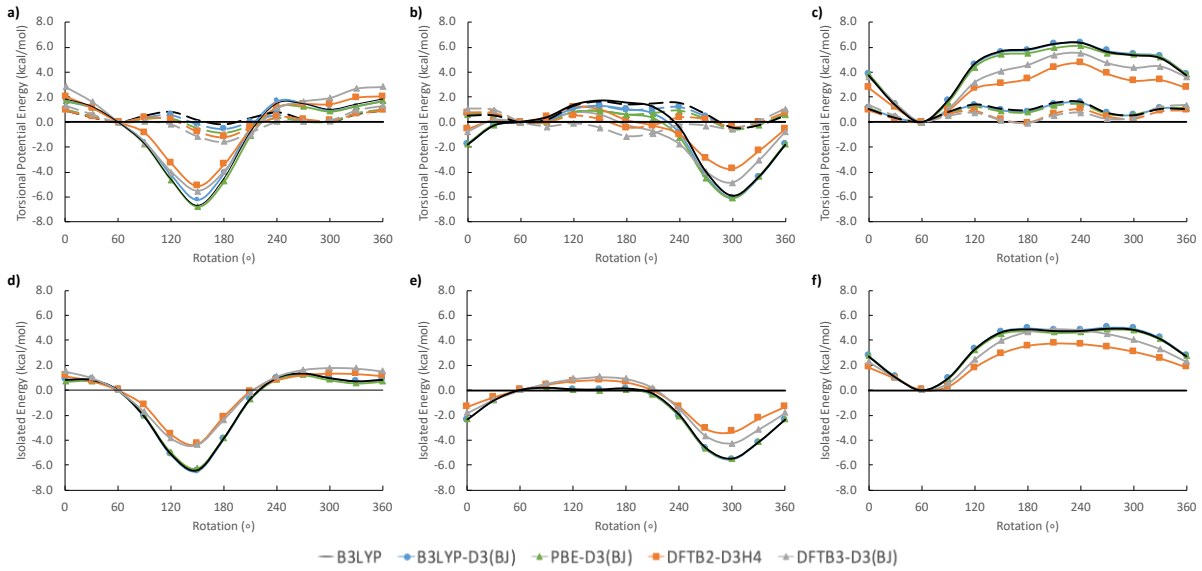


Figure S8. Torsional potential energy versus degree of rotation plots for 1,2- and 1,3-cyclohexanediol in vacuum. (From left to right) The energies of axial-axial, axial-equatorial, and equatorial-equatorial hydrogen bond interactions, respectively. (Top, a-c) The solid line represents the energy of a two hydroxyl group system and the dashed line represents the energy of a single hydroxyl group system. (Bottom, d-f) Isolated hydrogen bond energy.

Structure 33: B3LYP/6-311++G(d,p)-optimized geometry of allose, *α*-tg-(g-), 'cOcc'

24
Energy: -687.0967802

C	-1.04886	-0.51835	-0.62687
C	-0.88159	0.99170	-0.80678
C	0.58372	1.40462	-0.72937
C	1.22163	0.83839	0.53377
C	-0.26615	-1.02624	0.59961
C	-0.19615	-2.54463	0.66045
H	1.12834	0.99059	-1.58760
H	-0.74067	-0.64320	1.51312
H	-0.66401	-1.03177	-1.51045
H	-1.29169	1.29261	-1.77794
H	-1.20715	-2.95090	0.62132
H	-2.83680	-0.17442	0.02611
H	0.27022	-2.84121	1.60854
H	1.38292	-2.66859	-0.45373
H	0.73031	1.24846	1.42756
H	2.99157	0.89331	1.32445
H	1.52556	3.10641	-0.58476
H	-1.46959	2.55962	0.19634
O	1.10003	-0.57329	0.54024

O	-2.42188	-0.85806	-0.51706
O	-1.63350	1.60987	0.24249
O	0.61554	2.82798	-0.74142
O	2.57838	1.17802	0.50168
O	0.51413	-3.08784	-0.44447

Structure 34: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of allose, β-gg-(g+), 'rrrr'

24
Energy: -687.0951546

C	-1.04886	-0.51835	-0.62687
C	-0.88159	0.99170	-0.80678
C	0.58372	1.40462	-0.72937
C	1.22163	0.83839	0.53377
C	-0.26615	-1.02624	0.59961
C	-0.19615	-2.54463	0.66045
H	1.12834	0.99059	-1.58760
H	-0.74067	-0.64320	1.51312
H	-0.66401	-1.03177	-1.51045
H	-1.29169	1.29261	-1.77794
H	-1.20715	-2.95090	0.62132
H	-2.83680	-0.17442	0.02611
H	0.27022	-2.84121	1.60854
H	1.38292	-2.66859	-0.45373
H	0.73031	1.24846	1.42756
H	2.99157	0.89331	1.32445
H	1.52556	3.10641	-0.58476
H	-1.46959	2.55962	0.19634
O	1.10003	-0.57329	0.54024
O	-2.42188	-0.85806	-0.51706
O	-1.63350	1.60987	0.24249
O	0.61554	2.82798	-0.74142
O	2.57838	1.17802	0.50168
O	0.51413	-3.08784	-0.44447

Structure 35: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of altrose, α-tg-(g-), 'crcc'

24
Energy: -687.0958093

C	1.27207	-1.26985	0.77233
C	-0.12478	-1.50836	1.36399
C	-1.20601	-0.99213	0.40243
C	-0.93887	0.45916	-0.00470
C	0.52005	0.65118	-0.45181
C	0.88372	2.12111	-0.63312
H	2.04141	-1.48793	1.51313

H	-0.27466	-2.57702	1.52851
H	-2.18341	-1.05514	0.89130
H	-1.13123	1.10342	0.86398
H	0.67564	0.11911	-1.39815
H	1.94201	2.20990	-0.89143
H	0.71275	2.66137	0.30042
H	0.23046	-0.02850	2.57431
H	-1.68694	-1.37065	-1.44243
H	-1.59318	1.60173	-1.43896
H	0.44312	2.61886	-2.49114
H	0.69031	-2.18576	-0.82596
O	-0.23593	-0.87202	2.62973
O	-1.18581	-1.83644	-0.75768
O	-1.85982	0.75380	-1.05189
O	1.41463	0.14493	0.53993
O	0.04883	2.74685	-1.62255
O	1.53137	-2.03268	-0.36313

Structure 36: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of altrose, β-tg-(t), 'cOcc'

24
Energy: -687.0923077

C	1.26905	-1.33095	0.47701
C	-0.07453	-1.59662	1.16451
C	-1.23096	-1.05208	0.32088
C	-0.99773	0.40922	-0.08968
C	0.42133	0.58904	-0.65714
C	0.79781	2.04576	-0.88681
H	1.32881	-1.83477	-0.49092
H	-0.21116	-2.67057	1.29848
H	-2.15893	-1.11291	0.90219
H	-1.10294	1.05322	0.79686
H	0.49410	0.03814	-1.60417
H	1.80664	2.09563	-1.30722
H	0.78929	2.57497	0.07360
H	0.15397	-0.09164	2.38800
H	-1.88085	-1.40550	-1.46166
H	-1.75144	1.52723	-1.49622
H	0.02485	3.54471	-1.92113
H	2.12293	-1.56082	2.16996
O	-0.04607	-1.03236	2.47663
O	-1.31030	-1.87370	-0.83687
O	-2.01105	0.71213	-1.04121
O	1.38019	0.09409	0.27633
O	-0.16544	2.61157	-1.78872

O	2.34009	-1.74820	1.24564

Structure 37: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of galactose, *α*-gg-(g+),

'cccc'

24
Energy: -687.0979678

C	-0.44608	-1.54438	0.67238
C	0.90154	-0.92768	1.06059
C	0.82985	0.59926	1.07833
C	0.29021	1.11943	-0.25144
C	-1.03536	0.41553	-0.57451
C	-1.58377	0.73979	-1.95746
H	-0.33745	-2.61827	0.49225
H	1.64646	-1.24220	0.32169
H	0.16613	0.91387	1.88719
H	0.08726	2.19616	-0.16051
H	-1.77194	0.72896	0.17516
H	-1.67605	1.82039	-2.08111
H	-2.57405	0.28810	-2.06991
H	1.96858	-0.90160	2.68354
H	2.61490	1.13807	0.55501
H	0.91522	0.79893	-2.08613
H	-0.96661	-1.41282	2.52418
H	-0.66474	-0.67609	-2.92540
O	1.23067	-1.43048	2.35434
O	2.11185	1.14223	1.38170
O	1.32295	0.90674	-1.21209
O	-0.90448	-1.01320	-0.54480
O	-0.70669	0.28609	-2.99561
O	-1.41659	-1.30746	1.67398

Structure 38: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of galactose, β-gt-(g-),

'rrrr'

24
Energy: -687.0928537

C	-0.36706	-0.91337	-0.79706
C	1.22590	-0.38317	0.89461
C	0.51137	0.92179	1.22659
C	-0.97739	0.77258	0.94773
C	-1.21581	0.32378	-0.49564
C	-0.39346	-1.32140	-2.26193

H	-0.75285	-1.74567	-0.18882
H	-1.38504	0.01363	1.63024
H	-1.35021	2.39055	1.96007
H	0.00596	-0.50247	-2.86684
H	1.23272	-2.36797	-2.18770
H	-1.42379	-1.51085	-2.56909
H	-2.27388	0.04360	-0.60107
H	-1.26184	2.17499	-1.04142
H	0.93239	1.69917	0.57959
H	1.57736	1.39622	2.79068
H	0.84524	-1.20101	1.52953
H	3.06039	-1.00705	0.98161
O	1.01704	-0.70840	-0.46789
O	2.59028	-0.17601	1.11116
O	0.64018	1.27413	2.60076
O	-1.66338	2.00697	1.13165
O	-0.89142	1.36095	-1.40713
O	0.32693	-2.52833	-2.47594

Structure 39: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of glucose, α-gt-(g-), 'rrrr'

24
Energy: -687.0957090

C	-0.85216	0.70670	-0.39070
C	0.63980	1.02502	-0.31062
C	1.30309	0.09709	0.69683
C	1.03681	-1.36507	0.34181
C	-0.46559	-1.60903	0.16513
C	-1.56969	1.49704	-1.47081
H	-1.32128	0.90246	0.57859
H	1.09729	0.85571	-1.29646
H	0.88739	0.31300	1.68993
H	1.53778	-1.59185	-0.60208
H	-0.64955	-2.59144	-0.27726
H	-1.08284	1.30752	-2.43745
H	-1.49122	2.56031	-1.24642
H	1.71185	2.53332	0.26815
H	3.13550	-0.26168	1.25526
H	0.99399	-2.25544	2.06357
H	-1.94565	-1.83041	1.43101
H	-3.01855	0.22865	-1.66935
O	-1.03245	-0.68644	-0.73345
O	0.77917	2.38691	0.06898

O	2.69948	0.38252	0.68449
O	1.60251	-2.23817	1.31232
O	-1.03079	-1.53025	1.46378
O	-2.95327	1.17966	-1.52588

Structure 40: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of glucose, β-gg-(g+), 'rrrr'

24
Energy: -687.0937521

C	-1.05415	0.61830	-0.40581
C	0.39495	1.11286	-0.36391
C	1.14090	0.48639	0.80653
C	1.00764	-1.02719	0.78268
C	-0.47026	-1.40242	0.74043
C	-1.78962	1.04161	-1.67018
H	-1.58765	1.01349	0.47094
H	0.89382	0.82952	-1.29823
H	0.70080	0.85972	1.74289
H	1.48005	-1.42922	-0.12243
H	-0.97855	-1.04887	1.65231
H	-2.84278	0.74632	-1.57922
H	-1.73413	2.12558	-1.77017
H	1.25957	2.83586	-0.13652
H	2.98574	0.47267	1.42986
H	1.59483	-2.48611	1.93770
H	-1.17643	-0.47205	-2.71174
H	-1.47291	-3.05843	0.67043
O	-1.08977	-0.81860	-0.39510
O	-0.54767	-2.79213	0.62904
O	0.35076	2.52874	-0.23617
O	2.49921	0.90227	0.71648
O	1.64834	-1.52380	1.95272
O	-1.20426	0.48402	-2.83758

Structure 41: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of gulose, α-gg-(g+), 'rcrc'

24
Energy: -687.0952666

C	0.10461	1.55944	0.48289
C	-1.35302	1.08909	0.36101

C	-1.45675	-0.42047	0.60449
C	-0.49362	-1.15510	-0.34332
C	0.92587	-0.59045	-0.21239
C	1.92420	-1.14401	-1.21948
H	0.19790	2.60538	0.18418
H	-1.65976	1.28375	-0.66745
H	-2.47111	-0.74746	0.37098
H	-0.45788	-2.21144	-0.04088
H	1.29410	-0.84096	0.79057
H	1.93980	-2.23413	-1.16512
H	2.92586	-0.76993	-0.98227
H	-2.13022	1.48093	2.09234
H	-0.45251	-0.28776	2.28373
H	-0.32791	-1.10700	-2.29279
H	1.35319	1.82815	1.97721
H	1.58461	0.15265	-2.63065
O	-2.20997	1.83797	1.19883
O	-1.24032	-0.75646	1.97395
O	-1.04519	-1.02335	-1.64661
O	0.95772	0.84110	-0.38752
O	0.50334	1.39549	1.84063
O	1.57709	-0.81074	-2.56688

Structure 42: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of gulose, β-gg-(g+),

'rrrc'

24
Energy: -687.0944012

C	0.17964	1.37751	0.76395
C	-1.26967	0.91126	0.59733
C	-1.37242	-0.61270	0.65829
C	-0.40976	-1.23552	-0.35367
C	1.00227	-0.67359	-0.13389
C	2.03301	-1.15216	-1.14526
H	0.53981	1.14804	1.77239
H	-1.63101	1.24560	-0.38308
H	-2.39533	-0.91301	0.40491
H	-0.37089	-2.31795	-0.16806
H	1.32445	-0.99097	0.86672
H	2.05305	-2.24333	-1.16664
H	3.02456	-0.79141	-0.85342
H	-1.89449	2.36773	1.74021
H	-1.50981	-0.56893	2.58997
H	-0.20913	-0.98727	-2.27788

H	1.77273	0.23543	-2.48751
H	0.11127	2.98688	-0.29927
O	0.28859	2.76724	0.62494
O	-2.08219	1.42591	1.64946
O	-1.00853	-1.08909	1.94942
O	-0.94031	-0.96066	-1.64211
O	1.01119	0.76156	-0.20795
O	1.72211	-0.72826	-2.47805

Structure 43: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of idose, α-gg-(g+), 'cccc'

24
Energy: -687. 0961018

C	1.38117	-0.91065	0.74498
C	0.01045	-1.55418	1.03664
C	-0.97374	-1.28586	-0.11485
C	-1.02890	0.21525	-0.44551
C	0.38923	0.75854	-0.66853
C	0.44946	2.26685	-0.86661
H	1.99141	-0.92603	1.64637
H	1.47453	2.55565	-1.11814
H	0.15790	-2.63281	1.12639
H	-1.96899	-1.62181	0.19195
H	-1.60196	0.36059	-1.37491
H	0.79338	0.28037	-1.57027
H	-0.21051	2.57245	-1.68106
H	-0.95372	-0.25009	2.09900
H	-1.15902	-2.00467	-1.95336
H	-1.41928	1.76932	0.68128
H	1.45685	-1.92709	-0.91118
H	0.62076	2.74562	1.01042
O	-0.51590	-1.09918	2.26766
O	-0.50670	-2.03821	-1.24604
O	-1.70859	0.84078	0.64369
O	1.22623	0.48170	0.45226
O	2.08750	-1.58279	-0.26240
O	0.00517	2.97064	0.30048

Structure 44: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of idose, β-gg-(g+), 'cccc'

24
Energy: -687.0969777

C	1.44362	-0.75843	0.69654
C	0.15949	-1.58971	0.86422

C	-0.76907	-1.44764	-0.34715
C	-1.00970	0.03482	-0.66989
C	0.33767	0.75557	-0.80697
C	0.21178	2.25587	-1.03491
H	1.20145	2.68063	-1.22909
H	2.07044	-1.16460	-0.10390
H	0.44706	-2.63826	0.96573
H	-1.72578	-1.92473	-0.10966
H	-1.54636	0.11246	-1.62746
H	0.86176	0.31273	-1.66620
H	-0.43057	2.46009	-1.89395
H	-1.05820	-0.45084	1.86451
H	-0.77146	-2.26798	-2.13391
H	-1.66293	1.51898	0.42872
H	0.20122	2.77370	0.83863
H	1.54097	-0.69484	2.58924
O	2.18256	-0.75469	1.86415
O	-0.49406	-1.21515	2.07206
O	-0.12372	-2.09998	-1.44253
O	-1.81799	0.55909	0.38709
O	1.11616	0.60765	0.37744
O	-0.39416	2.90812	0.08937

Structure 45: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of mannose, α-gg-(g+),

'rccc'

24
Energy: -687.0948824

C	-0.39825	-1.52686	0.99904
C	1.06892	-1.09815	1.04435
C	1.20019	0.41206	0.84728
C	0.43830	0.84788	-0.39486
C	-1.03039	0.42620	-0.26809
C	-1.86156	0.74491	-1.50000
H	-0.45315	-2.61027	0.86804
H	-1.89910	1.82544	-1.65103
H	1.47338	-1.37015	2.02583
H	0.78177	0.92626	1.72104
H	0.87333	0.36280	-1.27172
H	-1.47442	0.92147	0.60414
H	-2.88593	0.38985	-1.33299
H	2.60546	-1.38388	-0.08930
H	2.67541	1.60880	0.44254
H	0.48639	2.52448	-1.41692

H	-1.88903	-1.44224	2.23892
H	-1.20867	-0.76477	-2.52844
O	1.74205	-1.80494	0.01273
O	2.59336	0.69058	0.72753
O	0.57848	2.27020	-0.49349
O	-1.09752	-1.00336	-0.11375
O	-0.98211	-1.11723	2.21877
O	-1.31121	0.18230	-2.68375

Structure 46: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of mannose, β-gg-(g+), 'cccc'

24
Energy: -687.0943346

C	-0.57178	-1.43408	1.05919
C	0.90952	-1.04186	1.16568
C	1.10346	0.45822	0.96595
C	0.39744	0.92841	-0.29616
C	-1.08166	0.52664	-0.22535
C	-1.87347	0.91429	-1.46534
H	-1.88749	2.00074	-1.57395
H	-1.11972	-1.05723	1.93244
H	1.26394	-1.32404	2.16524
H	0.66945	0.99150	1.82437
H	0.84783	0.44383	-1.16573
H	-1.54731	1.00248	0.65263
H	-2.90699	0.57051	-1.34046
H	2.49863	-1.42475	0.11791
H	2.62902	1.60327	0.60709
H	0.48984	2.62333	-1.28217
H	-1.25124	-0.56823	-2.55064
H	-0.06208	-3.15944	0.42889
O	-0.72901	-2.80825	1.03636
O	1.60588	-1.78769	0.17474
O	2.50668	0.69362	0.90587
O	0.58056	2.34662	-0.36494
O	-1.16653	-0.89471	-0.12435
O	-1.29707	0.39024	-2.65439

Structure 47: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of talose, α-gg-(g+), 'rcrc'

24
Energy: -687.0986630

C	0.10223	1.51047	0.93973
C	-1.26992	0.82618	1.02586
C	-1.10294	-0.70265	1.01951
C	-0.26889	-1.13339	-0.19387
C	1.07488	-0.39186	-0.16484
C	1.97427	-0.67496	-1.35982
H	-0.03155	2.57398	0.72970
H	2.14214	-1.74957	-1.45285
H	-1.74128	1.13218	1.96122
H	-0.55447	-0.98969	1.91985
H	-0.07826	-2.21273	-0.13241
H	1.60568	-0.70217	0.74458
H	2.94126	-0.18254	-1.21251
H	-1.83964	0.81007	-0.82815
H	-2.90846	-1.00786	0.38564
H	-0.41463	-0.80458	-2.12385
H	1.55336	1.83839	2.19295
H	1.27655	0.70787	-2.53888
O	-2.12034	1.27054	-0.02024
O	-2.34668	-1.37023	1.08219
O	-1.03049	-0.84483	-1.37411
O	0.88083	1.03103	-0.15000
O	0.75731	1.29590	2.17179
O	1.38301	-0.25037	-2.59325

Structure 48: B3LYP-D3(BJ)/6-311++G(d,p)-optimized geometry of talose, β-gg-(g+), 'ccrc'

24
Energy: -687.0994385

C	0.37886	1.39885	1.07565
C	-1.08230	0.91503	1.08700
C	-1.16041	-0.61682	1.05090
C	-0.34169	-1.15745	-0.12629
C	1.09115	-0.61133	-0.02812
C	1.99464	-1.03183	-1.18143
H	3.01471	-0.68479	-0.98948
H	0.88994	1.12412	2.00774
H	-1.55744	1.28194	1.99979
H	-0.71355	-1.00315	1.97286
H	-0.31655	-2.25344	-0.07540
H	1.53377	-0.99613	0.90567
H	-1.56216	1.00316	-0.79443
H	-2.95096	-0.66924	0.30627
H	-0.35136	-0.78064	-2.05276
H	2.00649	-2.11951	-1.27390

H	-0.26348	3.02331	0.33409
H	1.57676	0.43949	-2.38272
O	0.44539	2.77203	0.94677
O	-1.78893	1.51520	0.00200
O	-2.49343	-1.08579	1.04715
O	-1.00058	-0.74311	-1.33032
O	1.09602	0.81305	-0.02537
O	1.52409	-0.52360	-2.43501

First principles geometries vs. DFTB-D3 optimized geometries.

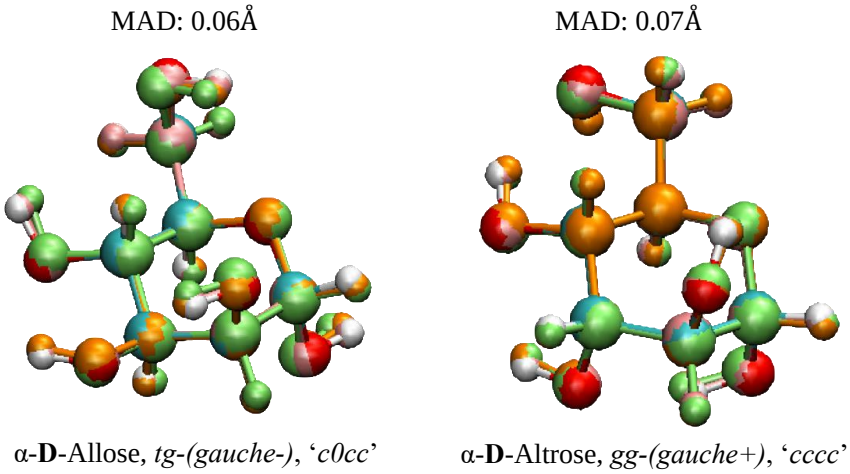


Figure S9. Comparisons of optimized structures including hydrogen atoms between optimized B3LYP (red, cyan, and white), B3LYP-D3(BJ) (pink), DFTB2 (orange), and DFTB2-D3H4 (lime) structures.

The geometry comparison of DFTB2, DFTB3, DFTB2-D3H4, and DFTB3-D3(BJ) structures with of the 170 B3LYP optimized structures studied in our investigation and their RMSD of atomic position distribution.

Table S5. The mean absolute deviation, root-mean square deviation, and the maximum deviation of RMSD of atomic position values (Å) for DFTB2, DFTB3, DFTB2-D3H4, and DFTB3-D3(BJ) versus optimized B3LYP geometries.

	Method			
	DFTB2	DFTB3	DFTB2-D3H4	DFTB3-D3(BJ)
All Atoms				
MAD	0.13	0.13	0.11	0.13
RMSD	0.14	0.14	0.12	0.14

MAX	0.38	0.39	0.38	0.40

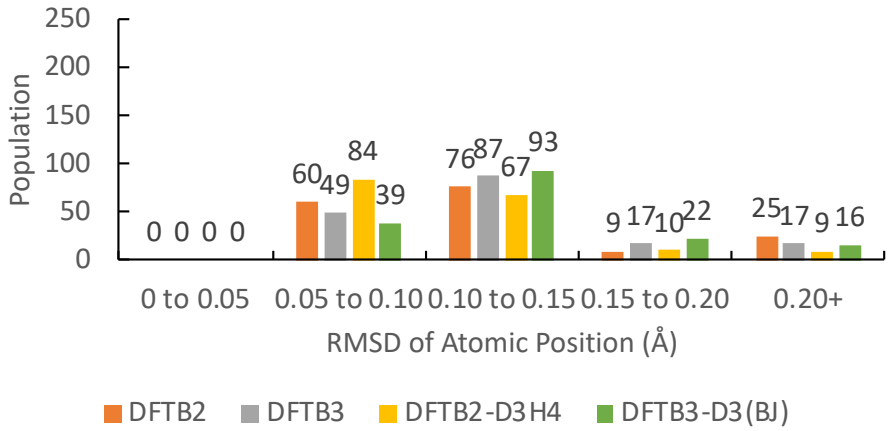


Figure S10. Distribution of geometries according to RMSD of atomic position values (hydrogen included) in vacuum with DFTB2-D3H4 and DFTB3-D3(BJ).

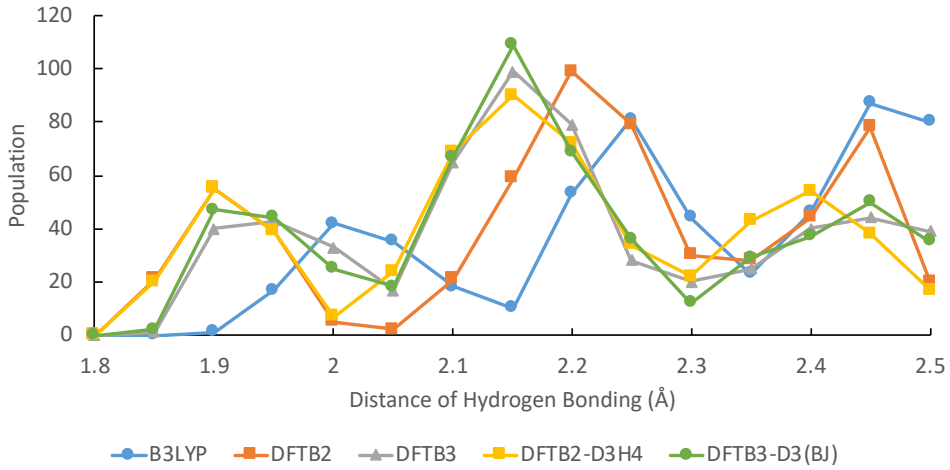


Figure S11. Distribution of hydrogen bonding distances in vacuum with DFTB2-D3H4 and DFTB3-D3(BJ).