

Supporting information on:

Dispersion forces in chirality recognition - a density functional and wave function theory study of diols

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1 DFT data

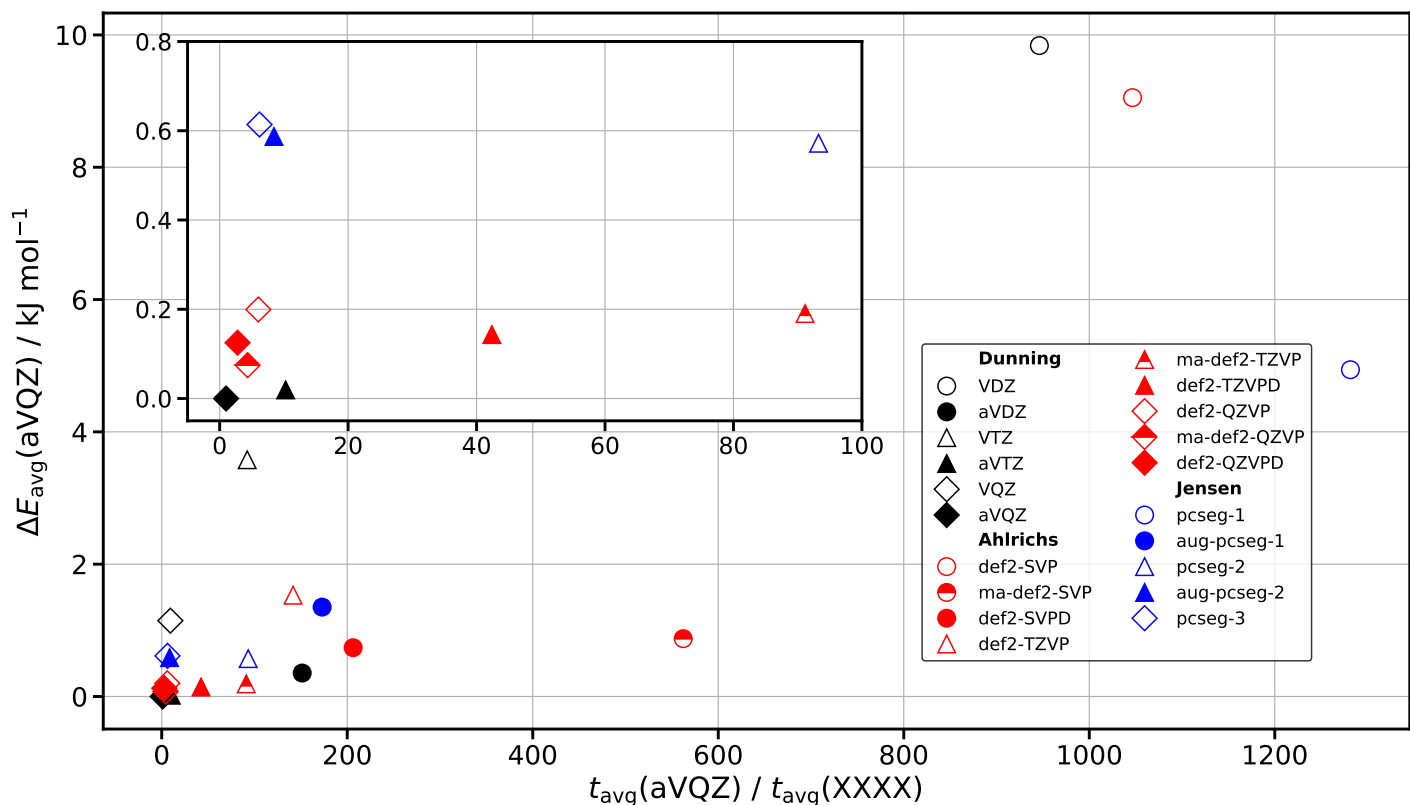
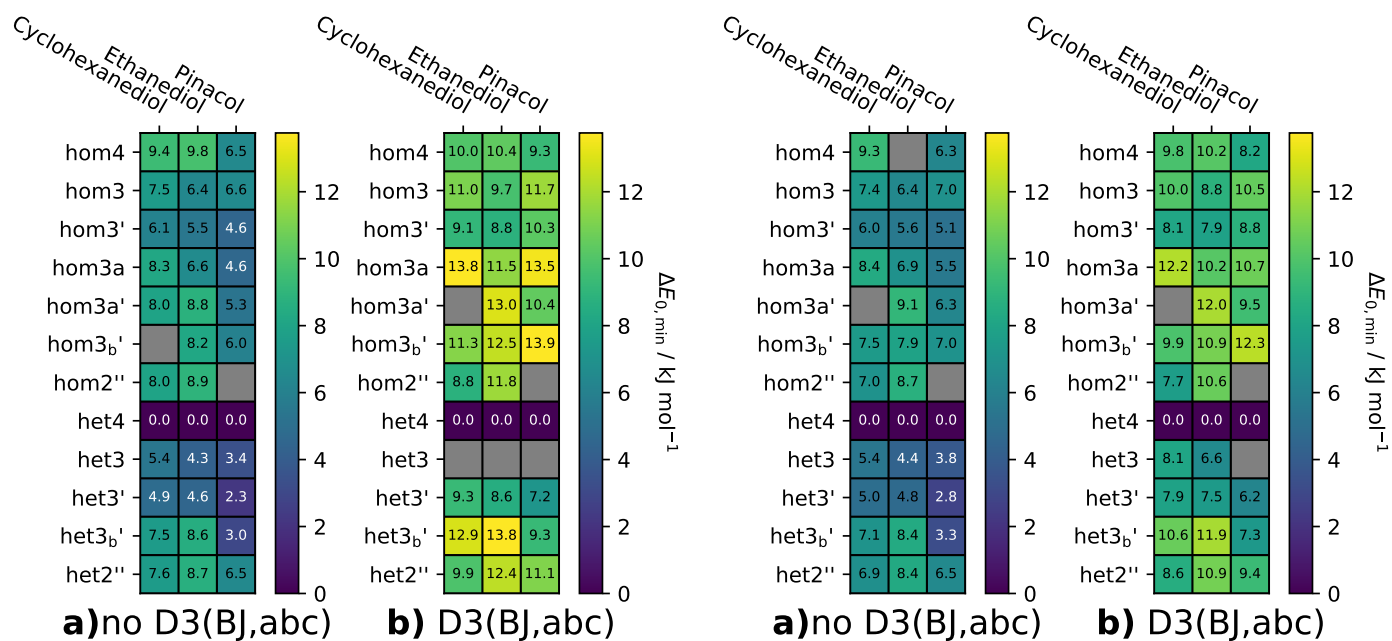
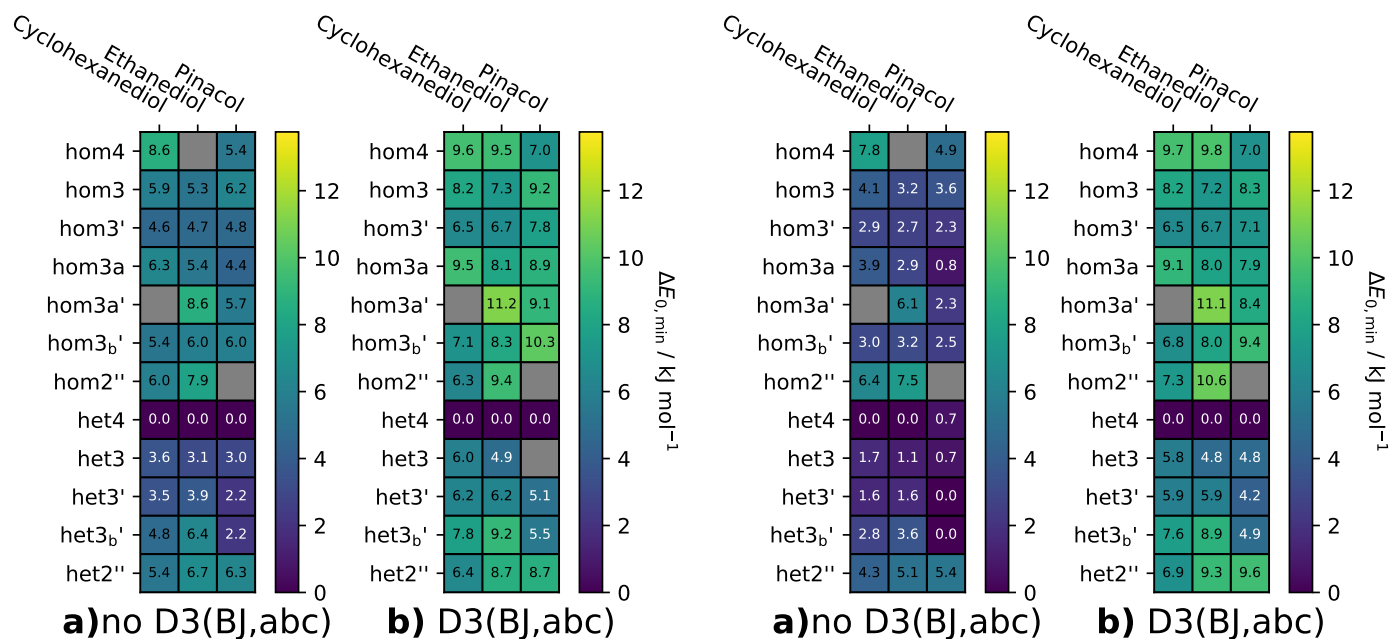


Fig. S1: Overview of the average energy difference relative to the Dunning aVQZ (aug-cc-pVQZ) basis set depending on the fraction of the computational time of aVQZ and each tested basis set. The fully augmented Dunning basis sets (aug-cc-pVXZ) as well as the non augmented variants (cc-pVXZ) were tested^[1,2]. Furthermore the def2-XZVP Ahlrichs^[3] family of basis sets were tested as well as the minimally augmented variants of Zheng et al.^[4] and the property optimized heavily augmented variants of Rappoport et al.^[5]. Additionally the augmented (aug-pcseg-X) and non augmented (pcseg-X) Jensen basis sets were tested^[6]. The aug-pcseg-3 calculations did not converge. All calculations were made for a total of 8 different ethanediol dimers and then averaged. For comparable timings each calculation was done on the same node.



(a) BP86

(b) PBE

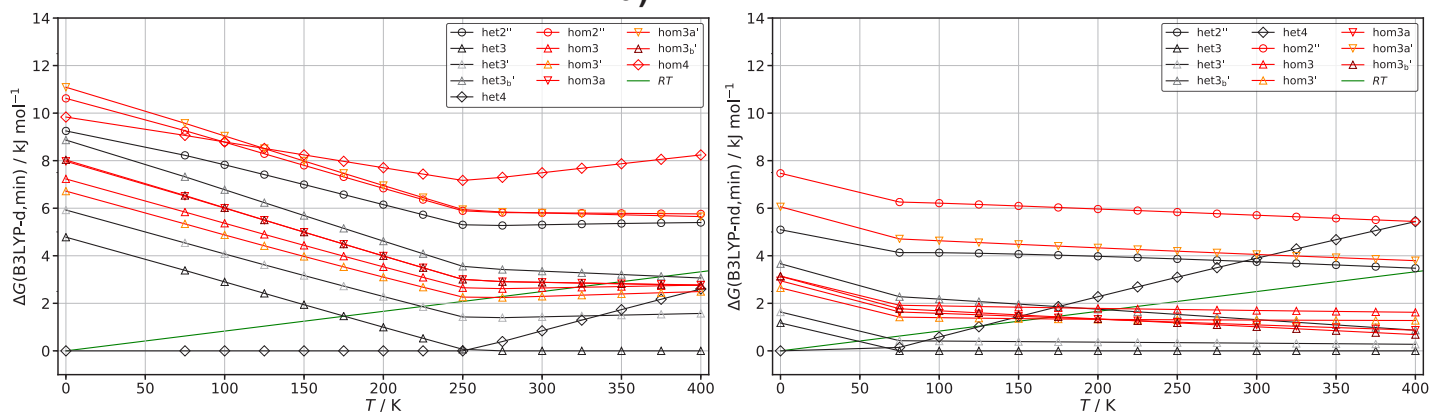


(c) PBE0

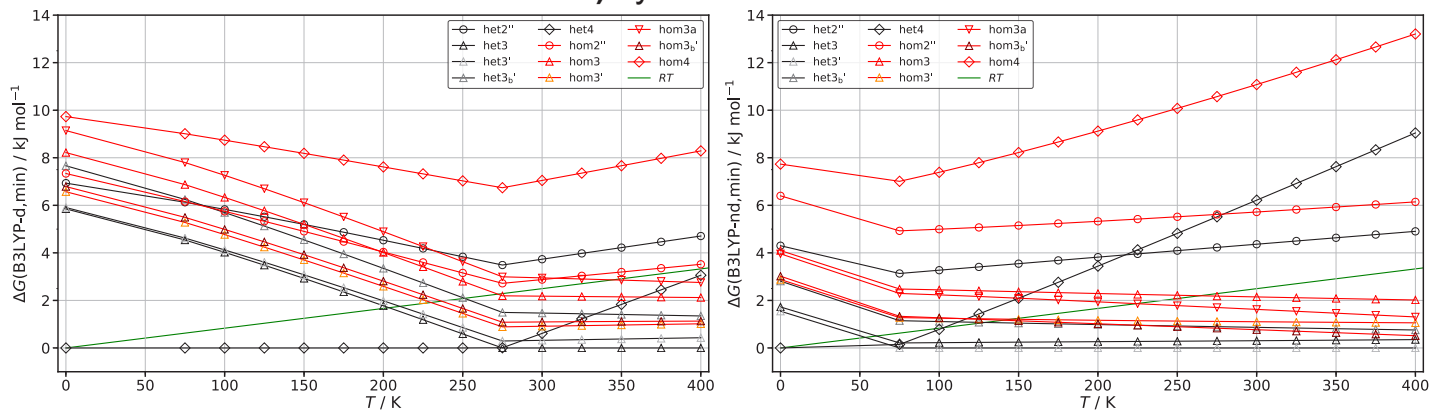
(d) B3LYP

Fig. S2: Overview of the DFT results with (b)) and without D3(BJ,abc) (a)) for cyclohexanediol, ethanediol and pinacol. The energies given are always relative to the minimum energy conformer and zero point corrected. Grey squares indicate unstable conformers.

a) ethanediol



b) cyclohexanediol



c) pinacol

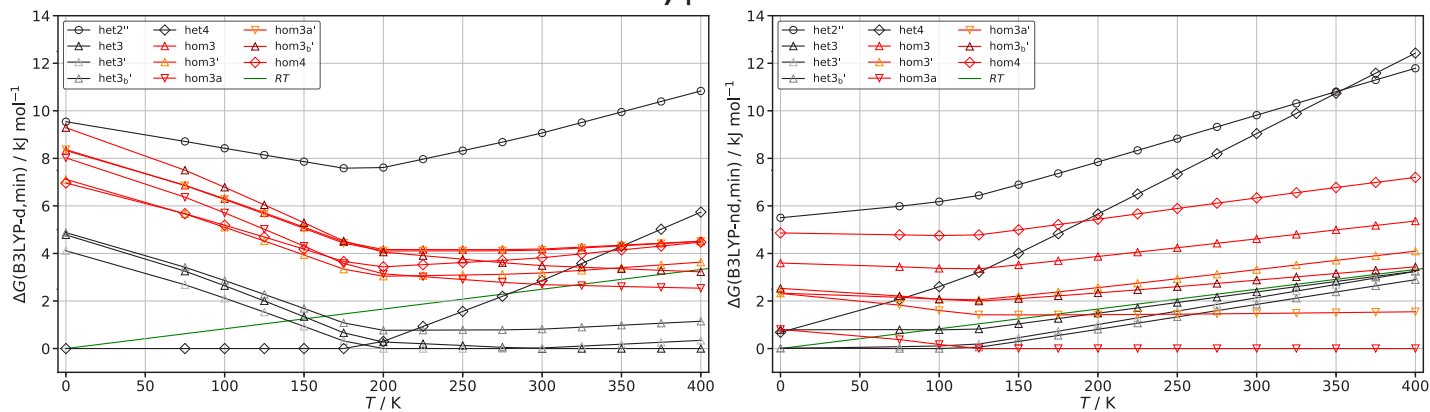


Fig. S3: Identical analysis as was done in Fig. 9 of the main text for ethanediol **a)**, cyclohexanediol **b)** and pinacol **c)** at the B3LYP level of computation.

2 WFT data

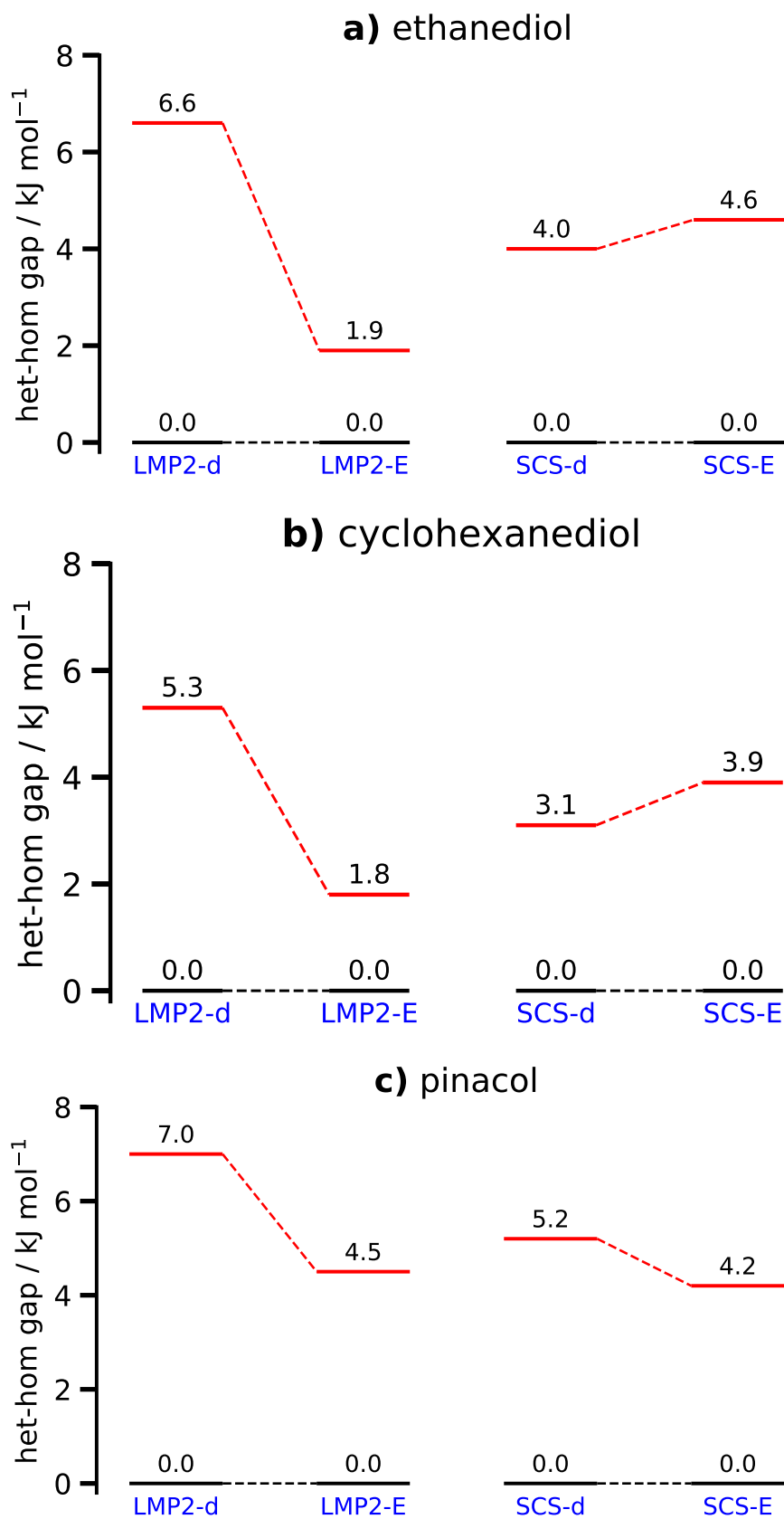


Fig. S4: Comparison of the LMP2-d and SCS-LMP2-d het-hom gap with the corresponding results purely based on the dispersion energy (LMP2-E and SCS-LMP2-E). The dispersion energy gap can also be inferred from Fig. 12 of the main text for SCS-LMP2 and figure S5 for LMP2.

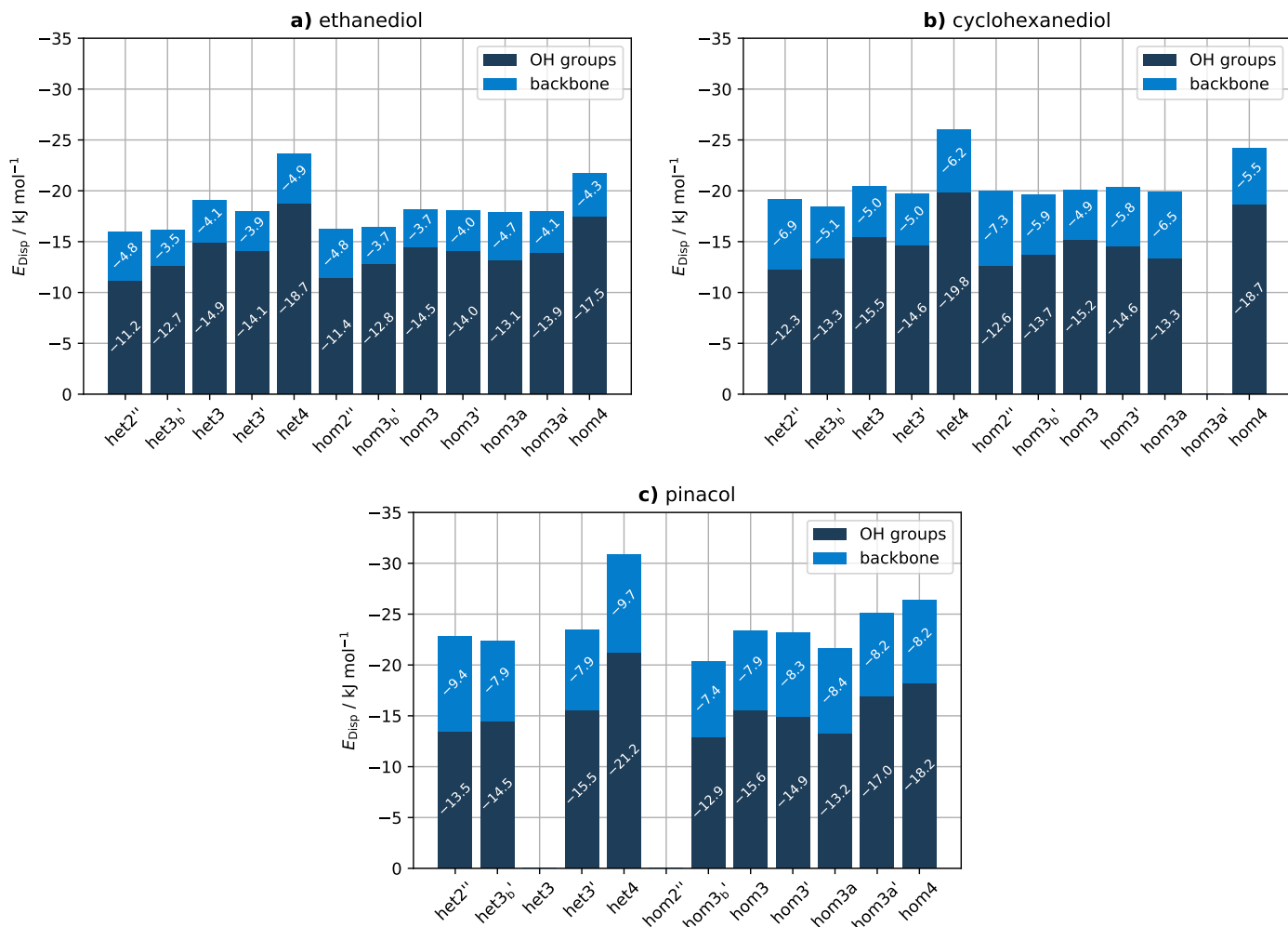


Fig. S5: Energy fragmentation of the dispersion energy at the LMP2-d level of computation for ethanediol (a), cyclohexanediol (b) and pinacol (c). A zero energy value indicates that a conformer either converges to a different one or exhibits an imaginary frequency. The performed analysis is analogous to that of Fig. 12 of the main text.

3 Geometry analysis data

3.1 Intermolecular hydrogen bond (Å), EDO

Tab. S1: Intermolecular H-bonding optimized at LMP2/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
	het2''	1.983	1.983			2.133	2.133	
het3 _b '	2.188	2.031	1.892		2.532	2.112	2.000	
het3	1.905	1.998	1.899		2.045	2.152	2.063	
het3'	1.928	1.976	1.920		2.085	2.131	2.100	
het4	1.959	1.959	1.959	1.959	2.111	2.111	2.111	2.111
hom2	1.926	1.973			2.081	2.145		
hom3a	1.841	1.972	2.065		1.956	2.215	2.244	
hom3a'	1.822	1.961	2.021		2.034	3.390	2.046	
hom3 _b '	2.145	1.983	1.886		2.491	2.083	2.006	
hom3	1.847	1.980	1.959		1.956	2.154	2.136	
hom3'	1.876	1.971	1.961		2.004	2.159	2.135	

Tab. S2: Intermolecular H-bonding optimized at B3LYP/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
het2''	1.939	1.939			1.980	1.980		
het3 _b '	2.141	1.988	1.876		2.203	2.046	1.915	
het3	1.881	1.973	1.865		1.925	2.008	1.911	
het3'	1.885	1.943	1.877		1.913	2.000	1.935	
het4	1.951	1.951	1.951	1.951	1.997	1.997	1.997	1.997
hom2''	1.898	1.932			1.957	1.977		
hom3a	1.810	1.926	2.018		1.832	1.998	2.091	
hom3a'	1.792	1.916	2.001		1.811	2.018	2.044	
hom3 _b '	2.062	1.956	1.864		2.114	2.024	1.909	
hom3	1.828	1.940	1.916		1.852	2.015	1.987	
hom3'	1.841	1.935	1.921		1.870	2.019	1.990	

Tab. S3: Intermolecular H-bonding optimized at SCS-LMP2/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
het2''	2.052	2.052			2.178	2.178		
het3 _b '	2.255	2.083	1.944		2.510	2.152	2.030	
het3	1.968	2.059	1.964		2.079	2.181	2.096	
het3'	1.997	2.038	1.992		2.119	2.161	2.133	
het4	2.024	2.024	2.024	2.024	2.144	2.144	2.144	2.144
hom2''	1.992	2.051			2.116	2.196		
hom3a	1.897	2.051	2.140		1.987	2.250	2.288	
hom3a'	1.866	2.075	2.102		2.063	3.474	2.073	
hom3 _b '	2.232	2.031	1.937		2.499	2.112	2.035	
hom3	1.900	2.044	2.026		1.986	2.183	2.169	
hom3'	1.936	2.039	2.025		2.035	2.188	2.166	

3.2 Intermolecular hydrogen bond (Å), CHexDO

Tab. S4: Intermolecular H-bonding optimized at LMP2/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
het2''	2.002	2.002			2.175	2.175		
het3 _b '	2.176	2.002	1.873		2.378	2.131	2.007	
het3	1.910	1.988	1.898		2.089	2.139	2.077	
het3'	1.960	1.956	1.921		2.140	2.122	2.106	
het4	1.939	1.939	1.939	1.939	2.099	2.099	2.099	2.099
hom2''	2.013	1.947			2.196	2.142		
hom3a	1.869	1.907	2.065		2.011	2.203	2.301	
hom3 _b '	2.174	1.957	1.880		2.415	2.087	2.024	
hom3	1.866	1.952	1.942		1.987	2.153	2.159	
hom3'	1.923	1.959	1.948		2.055	2.172	2.173	

Tab. S5: Intermolecular H-bonding optimized at B3LYP/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
het2''	1.959	1.959			2.007	2.007		
het3 _b '	2.137	1.961	1.853		2.175	2.036	1.908	
het3	1.877	1.950	1.849		1.921	2.005	1.926	
het3'	1.912	1.922	1.868		1.947	1.986	1.939	
het4	1.928	1.928	1.928	1.928	1.988	1.988	1.988	1.988
hom2''	1.967	1.915			2.015	2.002		
hom3a	1.830	1.930	2.005		1.851	2.010	2.079	
hom3 _b '	2.102	1.925	1.850		2.124	2.007	1.905	
hom3	1.834	1.913	1.896		1.860	2.009	1.993	
hom3'	1.860	1.917	1.907		1.898	2.017	2.003	

Tab. S6: Intermolecular H-bonding optimized at SCS-LMP2/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
het2''	2.071	2.071			2.215	2.215		
het3 _b '	2.232	2.060	1.928		2.386	2.166	2.035	
het3	1.976	2.050	1.965		2.120	2.167	2.109	
het3'	2.031	2.019	1.993		2.171	2.150	2.138	
het4	2.005	2.005	2.005	2.005	2.132	2.132	2.132	2.132
hom2''	2.091	2.015			2.248	2.174		
hom3a	1.935	2.046	2.142		2.045	2.229	2.344	
hom3 _b '	2.257	2.007	1.934		2.443	2.113	2.052	
hom3	1.916	2.020	2.016		2.014	2.182	2.192	
hom3'	1.985	2.028	2.019		2.085	2.197	2.204	

3.3 Intermolecular hydrogen bond (Å), Pinacol

Tab. S7: Intermolecular H-bonding optimized at LMP2/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
het2''	1.982	1.982			2.394	2.394		
het3 _b '	2.192	2.069	1.883		2.361	2.298	2.081	
het3'	1.975	1.980	1.995		2.223	2.207	2.256	
het4	1.963	1.963	1.963	1.963	2.185	2.185	2.185	
hom3 _b '	1.906	2.099	2.090		2.193	2.306	2.313	
hom4	1.887	1.887	2.343	2.343	2.091	2.091	2.733	2.733

Tab. S8: Intermolecular H-bonding optimized at B3LYP/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
het2''	1.965	1.964			2.066	2.066		
het3 _b '	2.173	2.014	1.853		2.226	2.138	1.937	
het3'	1.909	1.948	1.923		1.999	2.053	2.055	
het4	1.950	1.950	1.950	1.950	2.036	2.036	2.036	2.036
hom3 _b '	1.916	1.986	2.094		2.014	2.055	2.234	
hom4	1.864	1.878	2.462	2.181	1.966	1.975	2.788	2.359

Tab. S9: Intermolecular H-bonding optimized at SCS-LMP2/aug-cc-pVTZ,H=cc-pVTZ.

Molecular System	with dispersion				without dispersion			
het2''	2.054	2.054			2.430	2.430		
het3 _b '	2.232	2.144	1.948		2.364	2.331	2.109	
het3'	2.056	2.048	2.075		2.243	2.235	2.277	
het4	2.035	2.035	2.035	2.035	2.212	2.212	2.212	2.212
hom3 _b '	2.029	2.155	2.159		2.220	2.322	2.335	
hom4	1.953	1.953	2.473	2.475	2.113	2.113	2.758	2.757

3.4 Generation of density plots in Figure 4 of the main text.

To illustrate how the intermolecular O–H bond distance is affected once dispersion contributions are neglected, a kernel density estimate (KDE) plot was employed. This allows a nice visualization of the distribution of the O–H values we have and is analogous to a histogram. The data in KDE are represented using a continuous probability density curve in one or more dimensions.

Since the values of the O–H bond distances in the previous tables are within 3 decimal places, the bin width chosen to represent the data was 0.001. This permits each value to be represented in each bin, so higher frequency indicated in the plots are representatives of several repeated O–H bond distances. In this section, the analogous histogram is reflected so as to show how the data looks like before employing the continuous probability density curve via KDE.

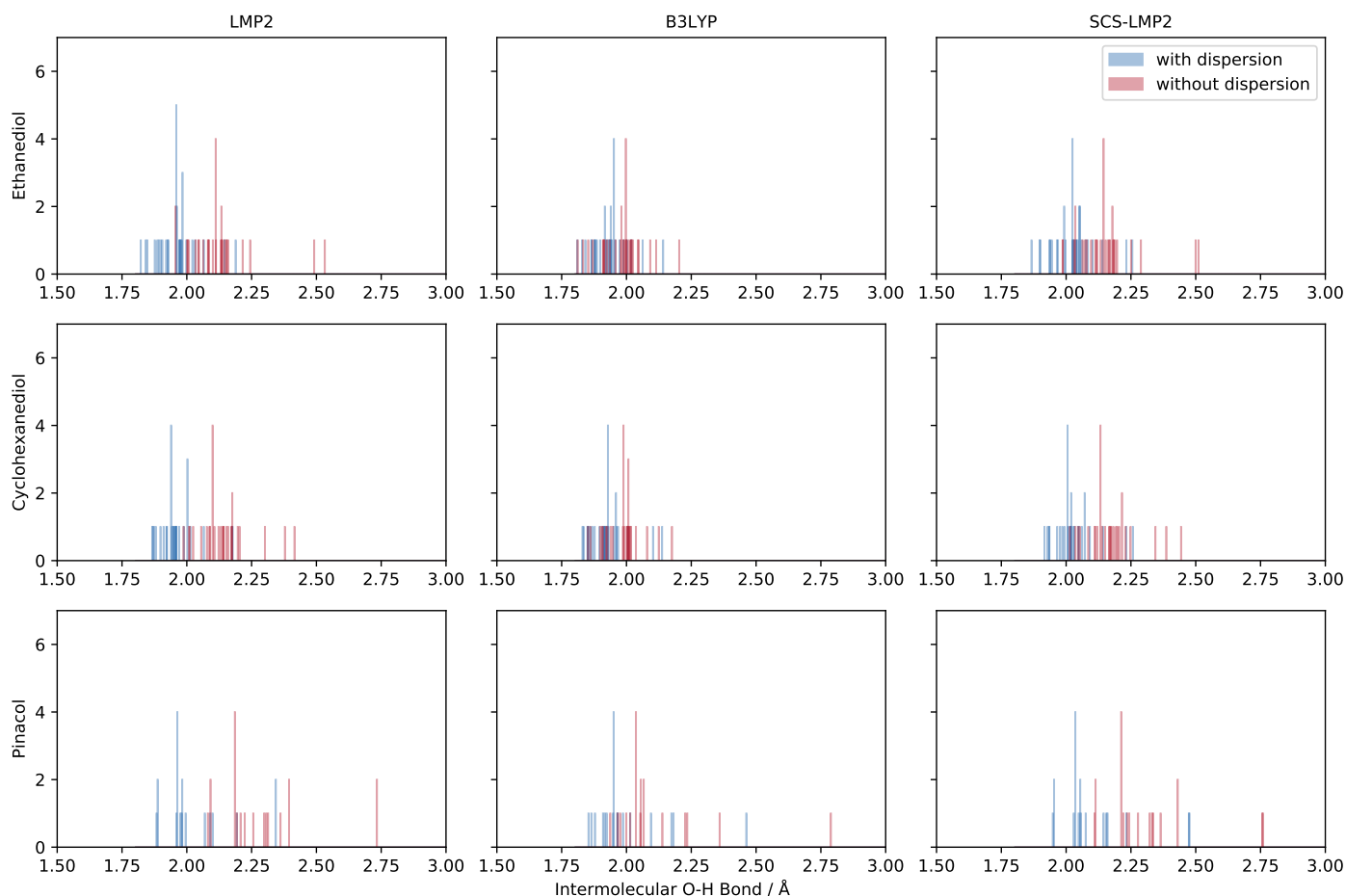


Fig. S6: Histogram counterpart of Figure 4 of the main text.

4 Structures

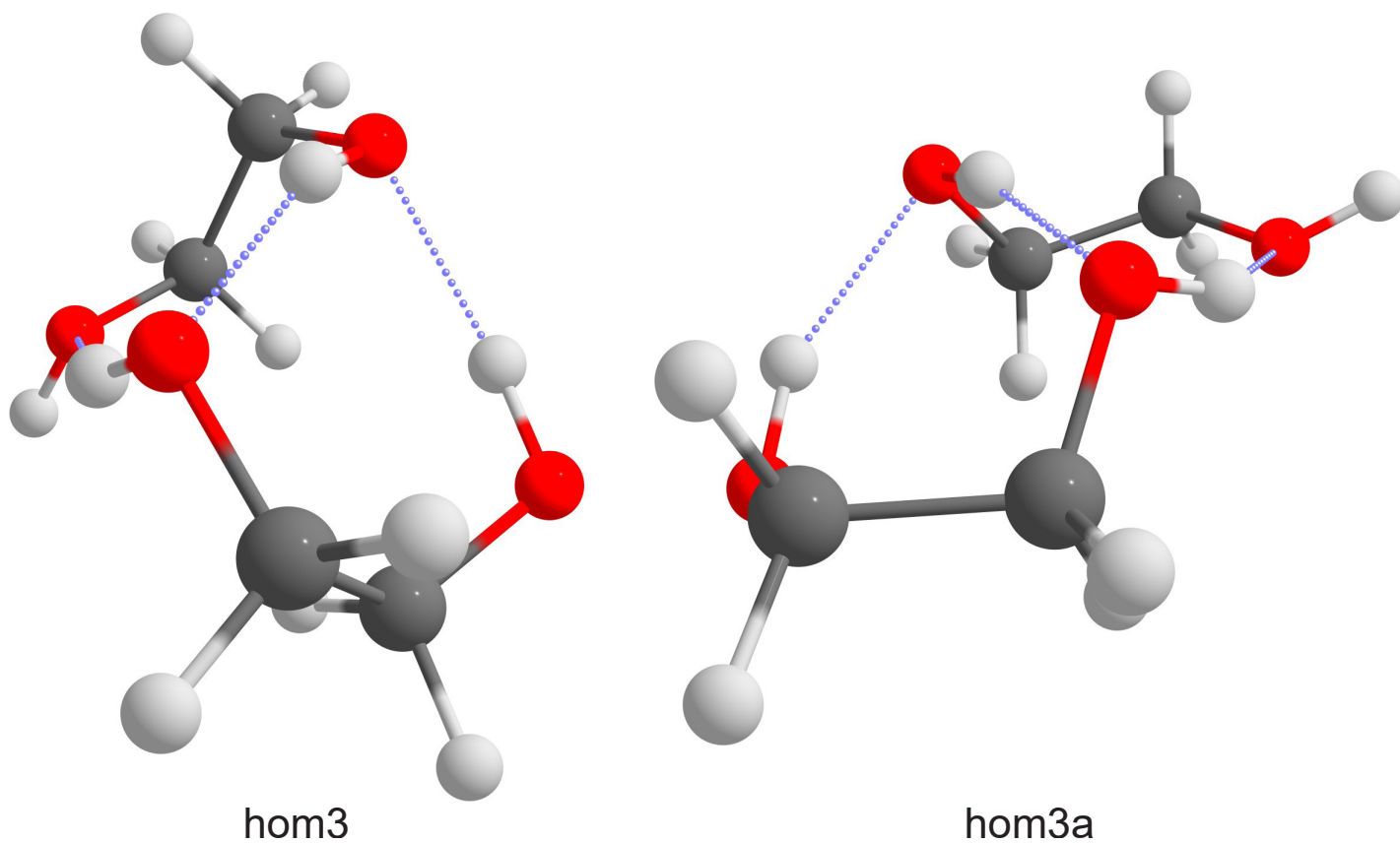


Fig. S7: Comparison of the more orthogonal arrangement of the C-C backbone of hom3 and the more parallel one of hom3a.

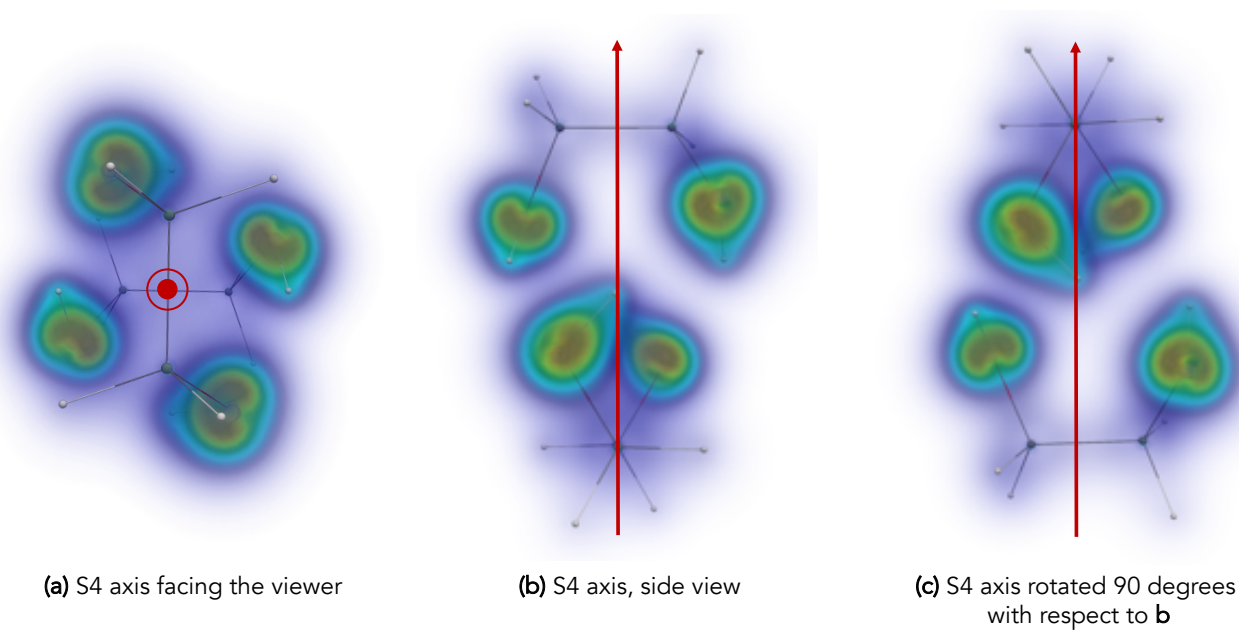


Fig. S8: Dispersion interaction density of het4 EDO viewed in different perspectives of its S_4 symmetry.

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