Supporting Information

Elucidation on the mechanism of the esterification of boric acid with aliphatic diols: a computational study to help set the record straight

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1. Computational Methods

Software

All the calculations were performed using the Gaussian 16 (G16) software [1] and GaussView [2] as graphical interface.

Geometry optimisations

All stationary state structures presented were the result of an optimisation followed by a frequency calculation terminated with "Stationary point found", indicating that the four convergence criteria (standard G16 thresholds) were met. Stationary states corresponding to a minimum on the PES had only real frequencies. Stationary states corresponding to a saddle point of order 1 on the PES (transition states, TSs) had only one imaginary frequency.

Reaction pathway discoveries

TSs were located via relaxed PES scans performed at the b3lyp/6-31++G(d,p) level of theory by including the bulk effect of the water solvent via the polarisable continuum model (PCM) [3]. Initial geometries were prepared based on chemical intuition or previously optimised structures, modified as required for the scan. All guess geometries used in the subsequent optimisations to a TS corresponded to a potential energy maximum along one internal coordinate. We noticed that the computational cost of systematically running several PES scans to determine these guess geometries was offset by the reduction to, typically, just two or three steps of the subsequent, significantly more computationally expensive, optimisation to a TS.

Newly discovered TSs were initially optimised at the b3lyp/6-31++G(d,p) level of theory in water solvent followed by IRC calculations at the same level of theory in water, performed in two separate runs for the forward and reverse path, to unambiguously identify the corresponding reactants and products.

Preliminary geometries of the reactant and product complexes, as well as separated reactants and products of each reaction pathway, were obtained by optimisation, at the same level of theory, in water, of the corresponding IRC minimum on the reactant and product side of each TS.

Final stationary state structures were obtained by optimisation of the preliminary geometries by employing the M06-2X functional by Zhao and Truhlar, [4] which corrects for dispersion effects implicitly and has been reported to be of good accuracy for small organic transition states involving non-covalent interactions [5] [6], together with the aug-cc-pvtz basis set, in water solvent. The bulk effect of the water solvent was included via the polarisable continuum model (PCM) [3].

Final geometries were extremely similar to the preliminary ones, despite these had been obtained without considering dispersion effects, and with a small, double-ζ basis set. The only notable exception is the geometry of TS3. At b3lyp/6-31++G(d,p) level, the tetrahydroxyborate anion (borate)

forms two hydrogen bonds with boric acid (BA) and one with the hydroxyl group of the 2(R),4(S)-pentanediol (2,4-PD). At the M062X/aug-cc-pvtz level the borate forms one additional hydrogen bond with the other hydroxyl group of 2,4-PD, further stabilising the TS.

Final energies were calculated, when practical, also at the CCSD(T)/aug-cc-pvtz//M062X/aug-cc-pvtz level of theory in water. Also in these calculations, the bulk effect of the water solvent was included via the polarisable continuum model (PCM) [3].

1.1 Optimised stationary state geometries.

Stationary state geometries were typically optimised as indicated in the G16 route section below, by including the bulk effect of the water solvent via the PCM.

Typical G16 route section for the optimisations to a minimum or a TS. The string “TheoryLevel” was either b3lyp/6-31++G(d,p) or M062X/aug-cc-pvtz.

```
# opt=calcfc freq=noraman TheoryLevel SCRF=(Solvent=Water)

# opt=(calcall,ts,noeigentest) nosymm TheoryLevel SCRF=(Solvent=Water)
```

Figures

Figures of the stationary state geometries were prepared with the open-source version of PyMOL. [7]

Figures not included in the main article are reported below.

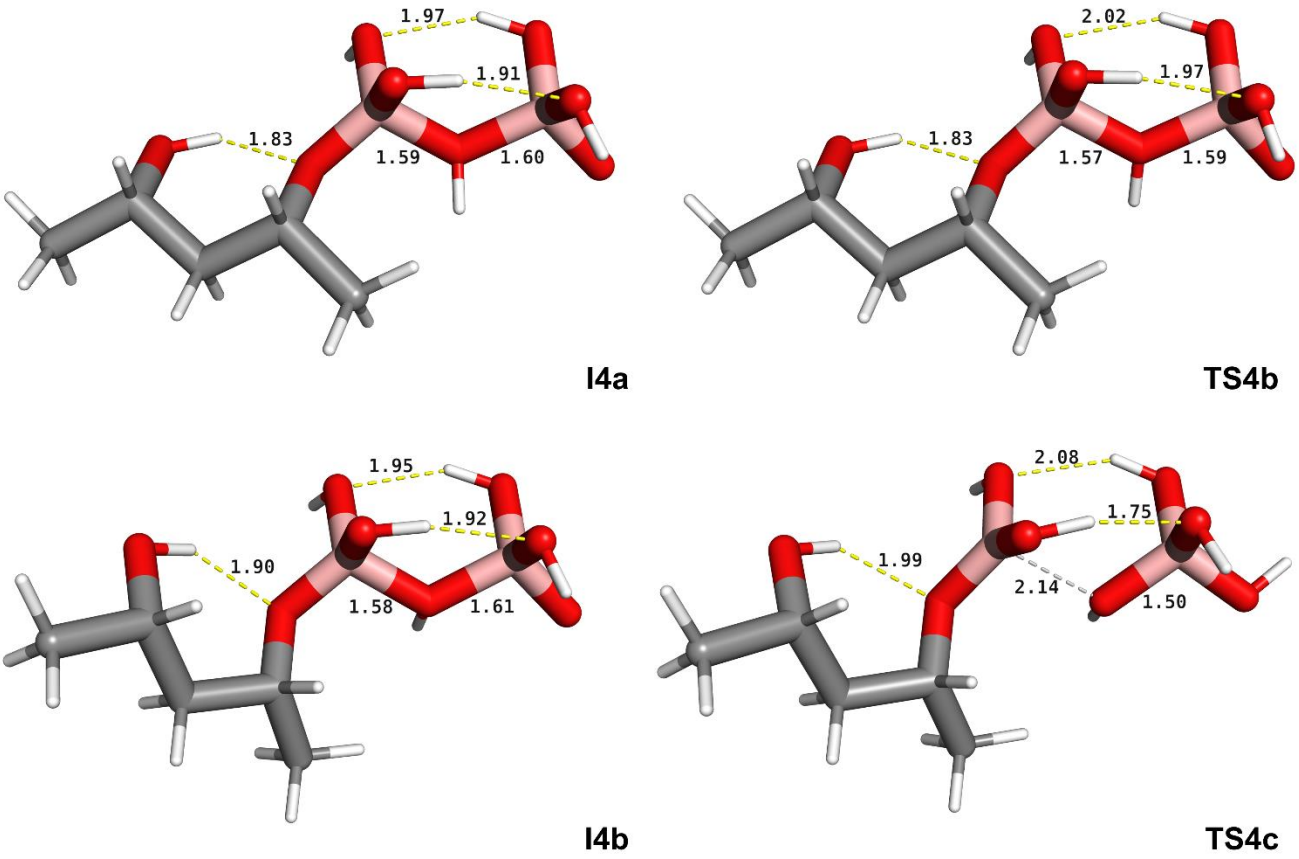

***Figure S1**. Structures of the of the stationary states following the initial, rate-determining step, TS4a (Figure 4), along the reaction pathway of the tetrahedral/trigonal exchange of the borate monoester, at M062X/aug-cc-pvtz level of theory in water solvent. Atom colours are C: grey, O: red, H: white, B: pink; chemical bonds forming and breaking are depicted as grey dashed lines, hydrogen bonds as yellow dashed lines, distances are in Å.*

Coordinates

Coordinates of the stationary state geometries are reported below in 18 data sections. Each section corresponds to the XYZ chemical file format of each geometry and reports the following information: number of atoms of the geometry; codename of the structure; sum of electronic and thermal Gibbs free energies (Ha) as obtained at the end of the successful G16 optimisation and frequency calculation ("Stationary point found"); table of the Cartesian coordinates.

```
3
 water    Energy: -76.433748
H     0.76103 -0.46945 -0.00000
O    -0.00000  0.11736  0.00000
H    -0.76103 -0.46945  0.00000

7
 BA    Energy: -252.506204
B     0.00001  0.00009  0.00000
O     0.98643  0.94556  0.00000
O    -1.31214  0.38136  0.00000
O     0.32575 -1.32695  0.00000
H     1.87099  0.57014  0.00000
H    -1.42978  1.33507 -0.00000
H    -0.44156 -1.90544  0.00000

9
 borate    Energy: -328.471617
O    -0.00000 -1.23484  0.80636
B     0.00000  0.00000  0.00000
O     0.00000  1.23484  0.80636
O     1.23484 -0.00000 -0.80636
O    -1.23484  0.00000 -0.80636
H    -0.86126 -1.34444  1.21309
H     0.86126  1.34444  1.21309
H     1.34444 -0.86126 -1.21309
H    -1.34444  0.86126 -1.21309
```

16

TS1a Energy: -580.966139

O	0.20202	-0.01165	0.96317
B	1.41786	-0.02597	0.06239
O	1.40830	-1.23012	-0.75207
O	1.29240	1.18339	-0.78165
O	2.65593	0.05973	0.82711
H	0.20670	-0.78320	1.53518
H	0.49638	-1.42125	-0.99629
H	1.60192	1.95070	-0.29494
H	2.93027	-0.81500	1.10701
B	-1.65111	0.04189	-0.05710
O	-2.53346	-0.04117	1.01381
O	-1.51137	-1.12921	-0.81307
O	-1.40880	1.26148	-0.65925
H	-2.61453	0.80422	1.46083
H	-1.83587	-1.89674	-0.33511
H	-0.45878	1.34213	-0.88746

16

I1a Energy: -580.972007

O	-0.00044	-0.00324	0.80368
B	-1.39646	0.03923	0.02514
O	-1.37836	1.27698	-0.69275
O	-1.44566	-1.12040	-0.85560
O	-2.42756	-0.06581	1.02232
H	-0.01806	-0.68344	1.48434
H	-0.46568	1.51266	-0.90742
H	-1.79231	-1.88480	-0.39013
H	-2.49867	0.75136	1.51938
B	1.39601	-0.02222	0.02457
O	2.42611	-0.13112	1.02353
O	1.44379	1.25860	-0.65963
O	1.37226	-1.13509	-0.87967
H	2.67976	-1.04845	1.13869
H	1.71745	1.95105	-0.05371
H	0.45877	-1.32276	-1.13470

16

TS1b Energy: -580.970268

O	0.00000	0.00000	0.75217
B	-1.40449	0.02689	0.02379
O	-1.37662	1.16675	-0.84925
O	-1.50233	-1.21903	-0.72170
O	-2.40834	0.09295	1.05340
H	-0.00000	0.00000	1.71078
H	-0.46071	1.40454	-1.04299
H	-1.72910	-1.94466	-0.13550
H	-2.53651	1.00039	1.33588
B	1.40449	-0.02689	0.02379
O	2.40835	-0.09297	1.05340
O	1.50235	1.21903	-0.72169
O	1.37661	-1.16674	-0.84927
H	2.53645	-1.00040	1.33592
H	1.72910	1.94466	-0.13548
H	0.46070	-1.40453	-1.04299

19

TS2 Energy: -657.398966

O	1.20263	1.32536	-0.00479
H	0.00106	1.33340	0.01320
B	1.86096	-0.09137	0.01390
O	1.31887	-0.71984	1.22121
O	1.49788	-0.83276	-1.15625
O	3.28402	0.16645	0.06407
H	1.65491	-0.28421	2.00760
H	0.53166	-0.89671	-1.23206
H	3.75193	-0.51798	-0.41703
O	-1.31831	-0.70617	-1.21784
B	-1.85974	-0.09103	-0.00336
O	-3.28280	0.16770	-0.05017
O	-1.49685	-0.84564	1.15832
O	-1.20073	1.32506	0.03100
H	-1.65151	-0.25915	-1.99904
H	-3.75030	-0.51957	0.42726
H	-0.53063	-0.91004	1.23380
H	-1.53836	1.83135	0.77605
H	1.54004	1.83961	-0.74446

19

2,4-PD Energy: -348.060945

C	-2.50149	-0.84440	0.09585
C	-1.26514	-0.08857	-0.35003
H	-2.55950	-0.86120	1.18663
H	-2.46911	-1.87433	-0.25718
H	-3.40030	-0.36899	-0.29385
C	0.01792	-0.71058	0.18756
O	-1.36397	1.29622	0.02106
H	-1.21855	-0.07241	-1.44086
C	1.29206	-0.05905	-0.33681
H	0.02817	-1.76665	-0.09095
H	0.01444	-0.66093	1.28217
C	2.53240	-0.80554	0.10760
O	1.41944	1.28514	0.12226
H	1.24969	-0.05798	-1.43359
H	2.56834	-0.85401	1.19691
H	3.42730	-0.29484	-0.24599
H	2.53209	-1.82061	-0.28771
H	-1.61330	1.34269	0.95094
H	0.54250	1.68724	0.06191

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TS3 Energy: -929.026766

C	-2.33110	1.36475	1.96026
C	-1.85654	0.65826	0.70339
H	-1.82955	0.94716	2.83539
H	-3.40655	1.24339	2.08680
H	-2.10027	2.42692	1.89765
C	-2.10230	-0.84673	0.76651
O	-0.46341	0.95958	0.52254
H	-2.37915	1.07282	-0.16076
C	-2.17947	-1.54258	-0.58776
H	-3.05861	-1.00598	1.26956
H	-1.33224	-1.31955	1.38191
C	-2.44975	-3.02510	-0.43256
O	-0.97674	-1.41352	-1.33523
H	-2.99917	-1.08630	-1.15665
H	-1.63636	-3.49230	0.12508
H	-2.52042	-3.50349	-1.40840
H	-3.38122	-3.19246	0.10683
H	0.32151	0.16578	0.87625
H	-0.78907	-0.47387	-1.51888
B	0.03230	1.86898	-0.63698
O	1.35273	2.32683	-0.21476
O	0.15600	1.08592	-1.84730
O	-0.95942	2.90599	-0.76072
H	1.27150	2.94067	0.51859
H	0.92266	0.49465	-1.75636
H	-0.94490	3.26789	-1.64829
O	1.84426	-1.04223	-1.03747
B	2.42664	-0.85778	0.28141
O	3.14002	-2.03004	0.74588
O	3.26639	0.30657	0.35518
O	1.17431	-0.65922	1.21744
H	1.01793	-1.53867	-0.99490
H	3.85058	-1.76666	1.33307
H	2.73364	1.08634	0.13587
H	1.45125	-0.51247	2.12648

25

PR3 Energy: -600.102320

C	-0.24650	2.65603	-0.04330
C	0.09283	1.18117	0.13109
H	-0.06379	2.95694	-1.07745
H	0.35940	3.28506	0.61048
H	-1.29885	2.81969	0.18431
C	1.55769	0.91676	-0.21819
O	-0.75900	0.40399	-0.67966
H	-0.05890	0.91625	1.18535
C	2.13212	-0.39447	0.31077
H	2.16648	1.72787	0.19191
H	1.66674	0.94571	-1.30765
C	3.61201	-0.51181	-0.00231
O	1.49598	-1.53903	-0.23447
H	2.00104	-0.39936	1.40217
H	3.76307	-0.49802	-1.08337
H	4.01201	-1.44674	0.38910
H	4.16944	0.31605	0.43485
H	0.55880	-1.53293	0.05256
B	-1.75081	-0.44274	-0.02357
O	-2.54920	-1.15025	-1.03254
O	-1.04441	-1.49113	0.76876
O	-2.58749	0.40659	0.84559
H	-3.18710	-0.54533	-1.41433
H	-1.53916	-2.31149	0.73173
H	-3.13111	-0.14750	1.40843

32

TS4a Energy: -852.594956

C	0.92539	2.35615	-0.22671
C	1.54752	1.04602	0.23629
H	0.81534	2.35583	-1.31312
H	1.55368	3.20107	0.05709
H	-0.05290	2.50117	0.23214
C	2.98167	0.90956	-0.26356
O	0.81279	-0.07509	-0.21938
H	1.56323	1.03970	1.33209
C	3.67985	-0.35866	0.21434
H	3.55419	1.77399	0.08022
H	2.98608	0.92299	-1.35908
C	5.14108	-0.38875	-0.18436
O	3.05801	-1.52169	-0.32600
H	3.60959	-0.39370	1.31010
H	5.23291	-0.30812	-1.26874
H	5.60170	-1.32414	0.13243
H	5.68316	0.43777	0.27431
H	2.10492	-1.31965	-0.33227
B	-0.55072	-0.33468	0.25598
O	-1.56974	0.27642	-0.67382
O	-0.79050	-1.79284	0.18938
O	-0.73091	0.14904	1.60605
H	-1.44325	1.22537	-0.74566
H	-0.48910	-2.13503	-0.65608
H	-1.67436	0.27093	1.75821
B	-3.56926	-0.11733	-0.16578
O	-4.23120	0.63151	-1.13164
O	-3.57851	0.42460	1.12662
O	-3.45936	-1.48845	-0.31277
H	-4.22912	0.18270	-1.97996
H	-3.79554	1.36033	1.11519
H	-2.57659	-1.79340	-0.02371

32

I4a Energy: -852.599872

C	0.69448	2.26185	-0.07933
C	1.41790	0.98171	0.31230
H	0.57756	2.30948	-1.16475
H	1.26102	3.13663	0.24009
H	-0.28716	2.31173	0.39391
C	2.84158	0.96207	-0.22968
O	0.74123	-0.16840	-0.17536
H	1.46095	0.92601	1.40479
C	3.63354	-0.28025	0.16209
H	3.36470	1.84393	0.14657
H	2.81648	1.03317	-1.32243
C	5.08992	-0.17613	-0.24092
O	3.09821	-1.44775	-0.45670
H	3.57271	-0.39496	1.25269
H	5.16801	-0.01299	-1.31703
H	5.61813	-1.09603	0.00826
H	5.57415	0.65297	0.27408
H	2.13369	-1.33483	-0.42928
B	-0.55096	-0.55357	0.35533
O	-1.63791	0.09464	-0.60674
O	-0.75032	-1.98554	0.21926
O	-0.79183	-0.10028	1.68757
H	-1.38546	0.97950	-0.88835
H	-0.44895	-2.29155	-0.63974
H	-1.70276	0.21373	1.76905
B	-3.20084	0.02974	-0.26214
O	-3.87998	0.75733	-1.29836
O	-3.39451	0.69568	1.01776
O	-3.50237	-1.36767	-0.20485
H	-3.88700	0.25272	-2.11400
H	-3.49319	1.64303	0.89893
H	-2.70857	-1.87296	0.01394

32

TS4b Energy: -852.599553

C	0.67936	2.24375	-0.14741
C	1.40377	0.97397	0.27256
H	0.61117	2.29192	-1.23677
H	1.22036	3.12379	0.20117
H	-0.32689	2.27044	0.26920
C	2.83883	0.95801	-0.23902
O	0.74615	-0.18789	-0.21530
H	1.42432	0.92796	1.36624
C	3.63376	-0.27025	0.18904
H	3.34643	1.85080	0.13280
H	2.83534	1.01108	-1.33314
C	5.09611	-0.16167	-0.19058
O	3.11845	-1.45346	-0.41703
H	3.55488	-0.36551	1.28035
H	5.19163	-0.01772	-1.26804
H	5.62729	-1.07242	0.08463
H	5.56473	0.68081	0.31712
H	2.15268	-1.34650	-0.41190
B	-0.53439	-0.59586	0.32713
O	-1.63528	0.13248	-0.52497
O	-0.72489	-2.02499	0.12487
O	-0.76219	-0.23198	1.69084
H	-1.34899	0.62878	-1.29406
H	-0.42902	-2.28994	-0.74941

H -1.63952 0.16109 1.78611
B -3.19170 0.07533 -0.22729
O -3.84368 0.80090 -1.28430
O -3.38207 0.73448 1.05510
O -3.52986 -1.31847 -0.16373
H -3.98163 0.23200 -2.04390
H -3.35575 1.68856 0.95100
H -2.73539 -1.84734 -0.01851

32
I4b Energy: -852.600111
C 0.95801 2.60665 -0.46418
C 1.29000 1.20376 0.01846
H 1.31294 2.74000 -1.48742
H 1.43701 3.35536 0.16771
H -0.11723 2.78003 -0.44366
C 2.79846 0.97975 0.05680
O 0.68690 0.23897 -0.83390
H 0.89985 1.06617 1.03184
C 3.20228 -0.43108 0.46909
H 3.23434 1.69539 0.75783
H 3.22431 1.18684 -0.93120
C 4.68681 -0.53930 0.74898
O 2.89354 -1.36953 -0.56054
H 2.64117 -0.69985 1.37290
H 5.25622 -0.22395 -0.12702
H 4.95494 -1.56929 0.98274
H 4.96619 0.09218 1.59173
H 2.01396 -1.11831 -0.88180
B -0.44858 -0.51689 -0.35038
O -1.64293 0.50654 -0.16777
O -0.82256 -1.48793 -1.36957
O -0.26379 -1.12375 0.92823
H -1.72056 1.07539 -0.94077
H -0.65590 -1.14178 -2.24953
H -1.08930 -1.09230 1.43049
B -3.10449 0.00852 0.29536
O -3.95384 1.16685 0.27513
O -2.90219 -0.48825 1.64245
O -3.51498 -1.00997 -0.62442
H -4.41906 1.22453 -0.56117
H -2.88821 0.23843 2.26963
H -2.74004 -1.44925 -0.99916

32
TS4c Energy: -852.594625
C 0.95129 2.53785 -0.44669
C 1.35077 1.16341 0.05624
H 1.27921 2.66532 -1.47945
H 1.41589 3.31444 0.16128
H -0.12948 2.65774 -0.40205
C 2.86309 0.98064 0.05012
O 0.74778 0.16716 -0.77333
H 0.98581 1.02201 1.07579
C 3.32099 -0.42250 0.43204
H 3.29025 1.70116 0.75087
H 3.26124 1.21442 -0.94293
C 4.79899 -0.46923 0.75837
O 3.10019 -1.34184 -0.63889
H 2.74568 -0.75172 1.30648
H 5.37897 -0.08887 -0.08407
H 5.11077 -1.49372 0.95876
H 5.01739 0.13900 1.63524
H 2.22931 -1.13606 -1.00076
B -0.25575 -0.66214 -0.28289
O -1.88111 0.72055 -0.17842
O -0.78620 -1.55338 -1.22222
O -0.31459 -0.99276 1.05148
H -1.96606 1.17690 -1.01933
H -0.61015 -1.26327 -2.12133
H -1.25279 -1.03522 1.33993
B -3.18825 0.08825 0.18350
O -4.18132 1.14538 0.33705
O -2.94769 -0.63331 1.46720
O -3.61444 -0.86625 -0.82922
H -5.06243 0.76799 0.30400
H -2.99555 -0.00590 2.19204
H -2.85211 -1.39748 -1.08103

23
PR4 Energy: -524.133683
C -0.71001 2.25518 -0.55264
C -0.11646 1.01781 0.09137
H -0.57888 2.21002 -1.63425
H -0.21060 3.14854 -0.17897
H -1.77256 2.33346 -0.32789
C 1.36654 0.87561 -0.20531
O -0.79307 -0.15534 -0.40295
H -0.26169 1.05646 1.17346
C 2.01329 -0.37426 0.38154
H 1.86549 1.75755 0.20101
H 1.52706 0.87687 -1.28790
C 3.52518 -0.29564 0.34393
O 1.63847 -1.54204 -0.34775
H 1.68447 -0.48227 1.42293
H 3.86440 -0.13182 -0.68006
H 3.96041 -1.22530 0.70834
H 3.88254 0.52389 0.96593
H 0.69020 -1.47871 -0.51063
B -2.02102 -0.51194 0.08118
O -2.67142 -1.59330 -0.44562
O -2.59518 0.19833 1.09596
H -2.19470 -2.01439 -1.16606
H -3.45269 -0.14804 1.35777

32
TS5 Energy: -852.606209
C 1.75877 -1.67724 2.24326
C 1.86233 -0.83521 0.98697
H 0.75560 -1.59299 2.66552
H 2.47835 -1.34403 2.99141
H 1.95236 -2.72528 2.01623
C 1.59695 0.64113 1.27105
O 0.93045 -1.32509 0.03571
H 2.87292 -0.92978 0.57128
C 1.57465 1.45713 -0.01374
H 2.36430 1.03347 1.94160
H 0.62649 0.73823 1.76936
C 1.21279 2.90990 0.22006
O 0.63828 0.87592 -0.92790
H 2.55707 1.39711 -0.48964
H 1.17954 3.45314 -0.72404
H 1.95405 3.38070 0.86544
H 0.23754 2.98760 0.70220
H -0.57298 1.05646 -0.55109
O -0.14843 -1.07784 -2.09926
O 2.20436 -0.72762 -1.89269
B 0.91051 -0.62247 -1.25213
O -2.70151 -0.91646 -0.87340
B -2.45323 -0.09440 0.29822
O -1.59431 -0.72862 1.23877
O -1.64323 1.20970 -0.19627
O -3.68852 0.38859 0.84747
H -3.43192 -0.57743 -1.39538
H -0.75548 -1.01675 0.84173
H -2.13666 1.71365 -0.85128
H -3.53121 0.89472 1.64688
H -1.02583 -1.04758 -1.68840
H 2.17112 -0.33002 -2.76469

22
PR5 Energy: -523.679760
C -2.83934 -0.73877 -0.14742
C -1.43961 -0.34641 0.28661
H -2.93182 -0.64353 -1.23104
H -3.58708 -0.09782 0.32131
H -3.04821 -1.77342 0.12556
C -1.11470 1.09868 -0.07729
O -0.51166 -1.21899 -0.31291
H -1.37286 -0.43804 1.38121
C 0.33022 1.43019 0.28005
H -1.79649 1.77979 0.43860
H -1.25212 1.23189 -1.15658
C 0.71770 2.82983 -0.15851
O 1.20318 0.50249 -0.31819
H 0.42533 1.36715 1.37519
H 1.75338 3.04088 0.10901
H 0.07780 3.57751 0.31177
H 0.61722 2.91989 -1.24184
O 1.75600 -1.74077 -0.89541
O 1.17333 -1.25089 1.37680
B 0.90518 -0.92296 -0.03242
H 1.67057 -1.43520 -1.80035
H 2.02590 -0.89018 1.62620

1.2 Optimised stationary state energies.

***Table S1**. Electronic energies (Ha), thermal corrections to 298.15 K (Ha) and imaginary frequencies (cm^{-1}) of the stationary states indicated by their respective codenames in this study. Levels of theory: M062X/aug-cc-pvtz (M062X); CCSD(T)/aug-cc-pvtz//M062X/aug-cc-pvtz (CCSD(T)).*

Codename	Theory level	Electronic energy / Ha	Thermal correction to Gibbs Free Energy / Ha	Im. Freq. / cm^{-1}
water	M062X	-76.43685908	0.003112	
water	CCSD(T)	-76.34875585		
BA	M062X	-252.52865481	0.022451	
BA	CCSD(T)	-252.18469044		
borate	M062X	-328.50346706	0.031851	
borate	CCSD(T)	-328.06892132		
TS1a, TS1c	M062X	-581.04216539	0.076026	-209.4963
TS1a, TS1c	CCSD(T)	-580.26423911		
I1a, I1b	M062X	-581.04847863	0.076472	
I1a, I1b	CCSD(T)	-580.27042659		
TS1b	M062X	-581.04656950	0.076301	-340.4460
TS1b	CCSD(T)	-580.26782797		
TS2	M062X	-657.49348053	0.094515	-576.5201
TS2	CCSD(T)	-656.62540625		
2,4-PD	M062X	-348.19923294	0.138288	
TS3	M062X	-929.26124969	0.234484	-538.5651
PR3	M062X	-600.27070700	0.168387	
TS4a	M062X	-852.80826273	0.213307	-198.3212
I4a	M062X	-852.81397253	0.214101	
TS4b	M062X	-852.81234777	0.212795	-335.7351
I4b	M062X	-852.81442036	0.214309	
TS4c	M062X	-852.80623117	0.211606	-187.4498
PR4	M062X	-524.29185314	0.158170	
TS5	M062X	-852.81930561	0.213097	-260.3391
PR5	M062X	-523.82657853	0.146818	

Energy diagrams

Gibbs free energy diagrams along the reaction pathways found have been prepared with mechaSVG, [8] an application for creating energy profile diagrams as Scalable Vector Graphics files and are reported in the figures below. Stationary states are indicated by their respective codenames.

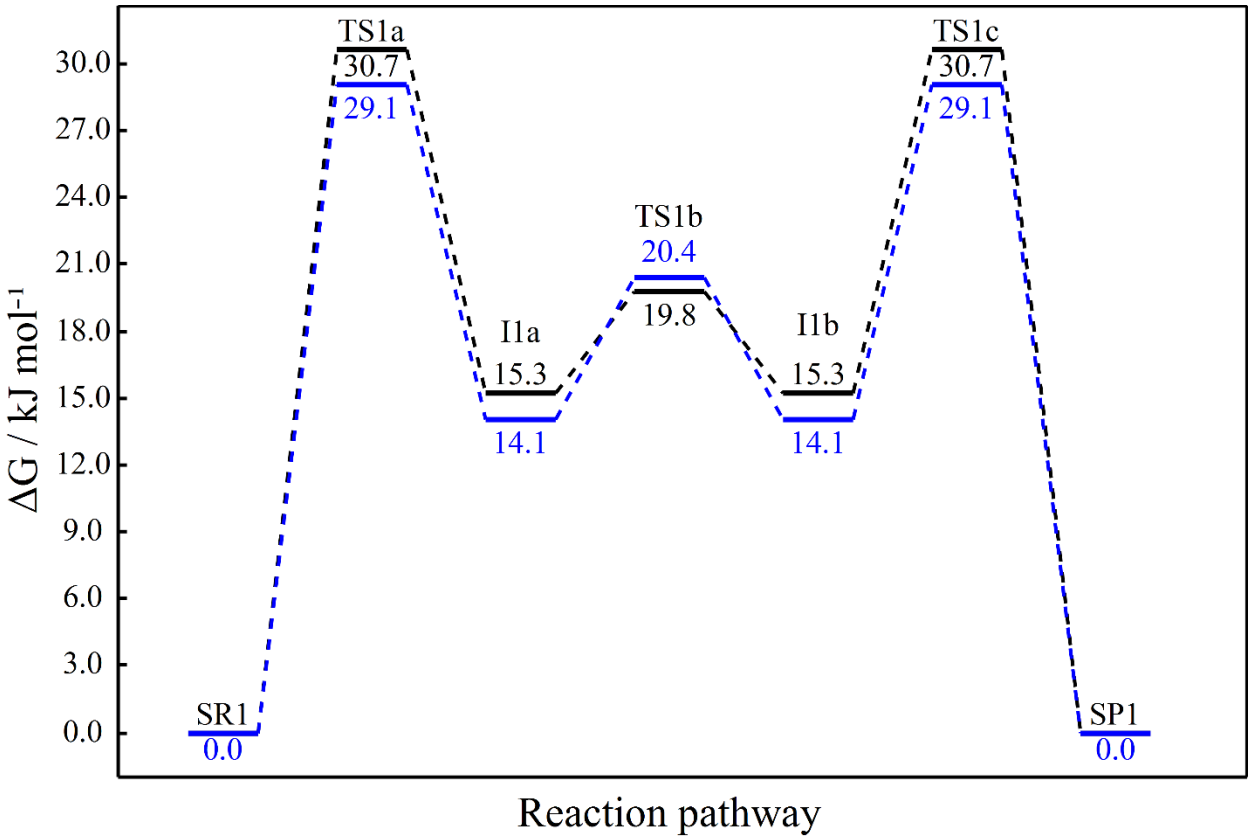

***Figure S2**. Gibbs free energy diagrams along the reaction pathway of the $B(OH)_3/B(OH)_4^-$ exchange calculated at two levels of theory in water solvent: M062X/aug-cc-pvtz (black); CCSD(T)/aug-cc-pvtz//M062X/aug-cc-pvtz (blue). In each diagram, the zero of the energy corresponds to the separated reactants (SR1) which, for this symmetric pathway, are the same as the separated products (SP1). Codenames of the stationary states are as in Figure 1.*

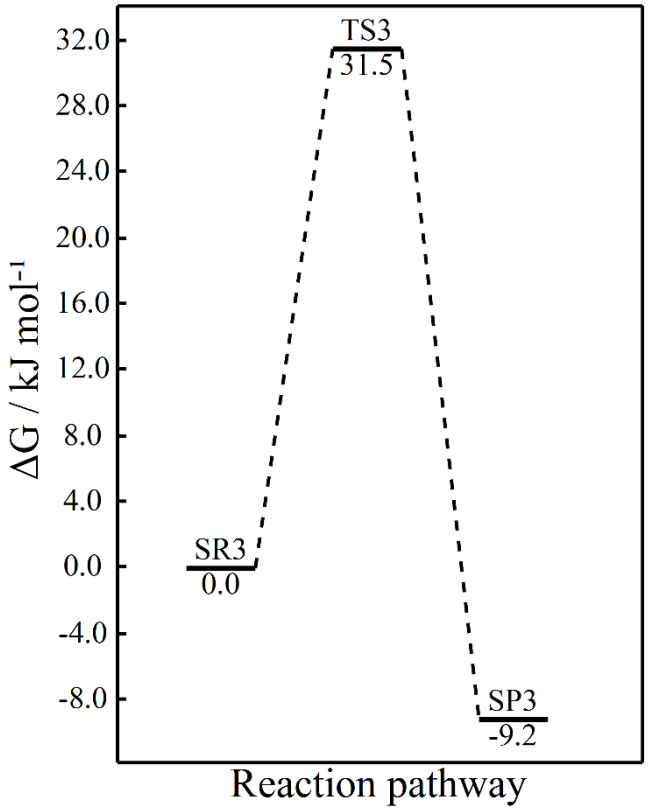

***Figure S3**. Gibbs free energy diagram across the TS of the first esterification step, TS3 (see Figure 3), between boric acid and 2(R),4(S)-pentanediol, calculated at M062X/aug-cc-pvtz level of theory in water solvent. The zero of the energy corresponds to the separated reactants (SR3).*

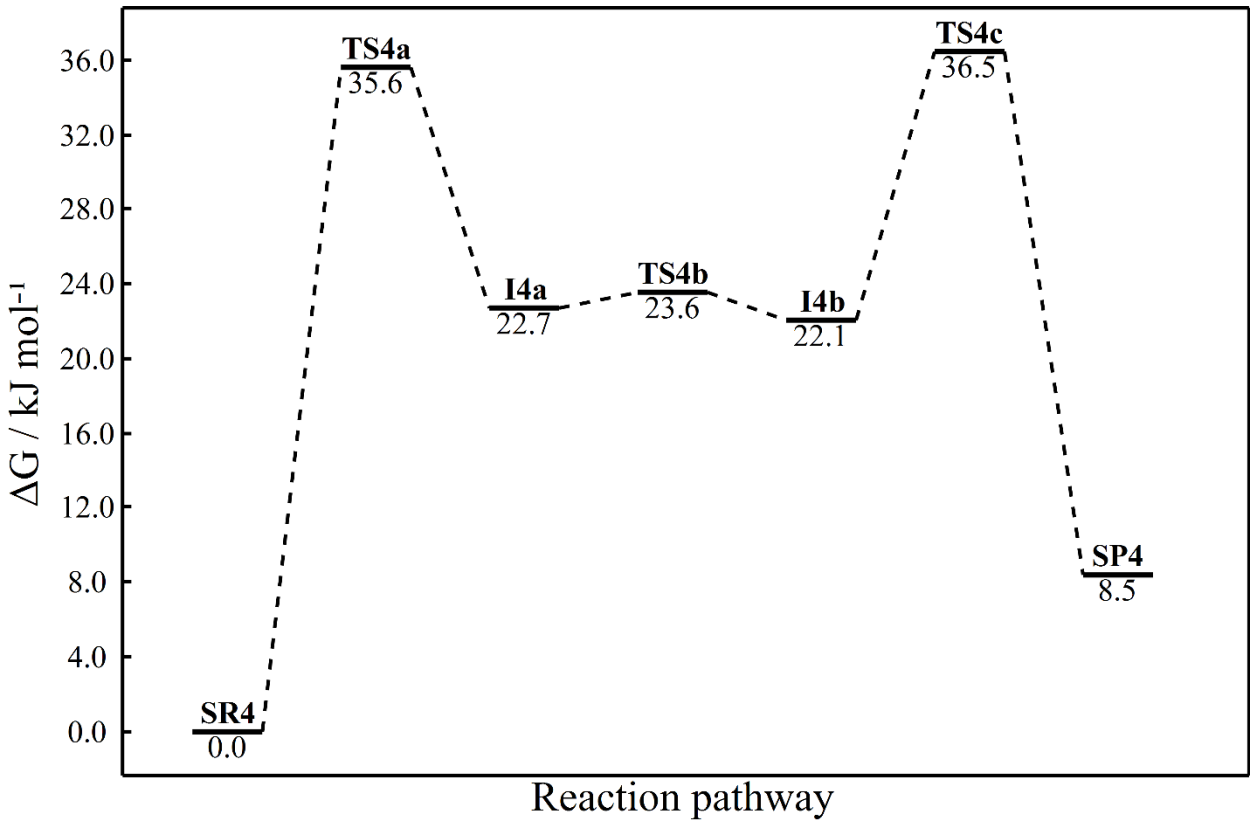

***Figure S4**. Gibbs free energy diagram along the reaction pathway of the tetrahedral/trigonal exchange of the borate monoester calculated at M062X/aug-cc-pvtz level of theory in water solvent. The zero of the energy corresponds to the separated reactants (SR4). The rate-determining step, TS4a, is depicted in Figure 4, the other stationary states are shown in Figure S1.*

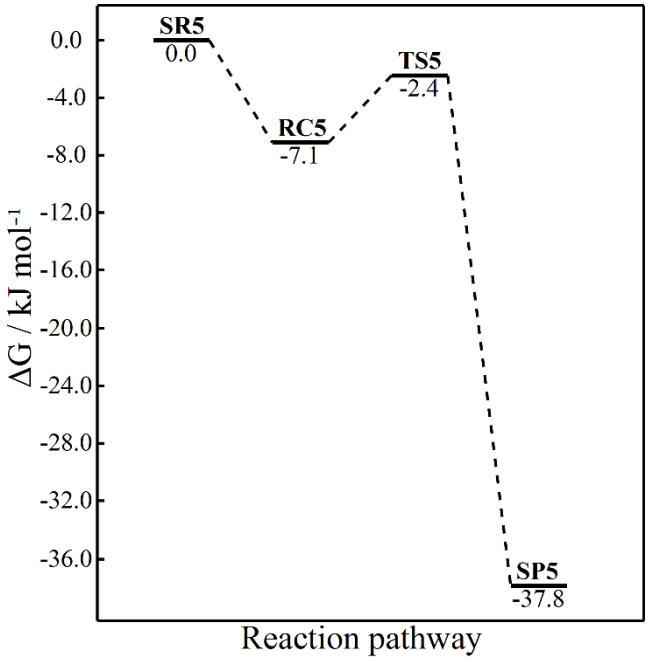

Figure S5*. Gibbs free energy diagram along the reaction pathway of the second esterification step between boric acid and 2(R),4(S)-pentanediol, calculated at M062X/aug-cc-pvtz level of theory in water solvent. The zero of the energy corresponds to the separated reactants (SR5). Structures of stationary states RC5 and TS5 are shown in Figure 5.*

1.3 $B(OH)_3/B(OH)_4^-$ exchange occurring through multiple pathways

The pathways along TS1a or TS2 describe parallel reactions. The pathway across TS2 features the same reactants as TS1a plus the solvent water. The overall rate constant of the $B(OH)_3/B(OH)_4^-$ exchange occurring through multiple pathways is given by the sum of the rate constants of the parallel reactions [9]. The Gibbs energies of activation of TS1a and TS2 are 29.1 kJ mol^{-1} and 36.9 kJ mol^{-1}, respectively. The corresponding rate constants, estimated with the Eyring equation, at 298.15 K, are 4.96×10^7 M^{-1}s^{-1} and 2.13×10^6 M^{-1}s^{-1}. The sum is 5.17×10^7 M^{-1}s^{-1}. The overall Gibbs energy of activation, associated with this overall rate constant, estimated with the Eyring equation, at 298.15 K, is 29.0 kJ mol^{-1}, very similar to the Gibbs energy of activation of the faster exchange pathway alone, i.e. the one across TS1a, of 29.1 kJ mol^{-1}. If the Gibbs energy of activation of TS2 were the same as TS1a, the overall Gibbs energy of activation would have been 27.4 kJ mol^{-1}, about 6% different from the Gibbs energy of activation of the faster exchange pathway alone (TS1a) and still in agreement with the experimental values of 20.5 ± 0.8 kJ mol^{-1} [10] and 36.5 kJ mol^{-1} [11].

1.4 IRC calculations and animations

IRC calculations were performed in two separate runs for the forward and reverse path for all the TSs studied. All calculations ended with “PES minimum detected on this side of the pathway”. The following route section was typically used:

```
# irc=(Forward,MaxPoints=400,RCFC,RecalcFC=(Predictor=5,Corrector=5),ReCorrect=Always) b3lyp/6-31++G(d,p) Geom=AllCheck Guess=Read SCRF=(Solvent=Water)
```

When initial convergence could not be achieved due to, e.g., a fairly flat PES around the TS, the following route section was typically used:

```
# irc=(Forward,MaxPoints=400,Stepsize=20,LQA,RCFC,RecalcFC=(Predictor=2,Corrector=2)) b3lyp/6-31++G(d,p) Geom=AllCheck Guess=Read SCRF=(Solvent=Water)
```

Wen convergence could not be achieved along the path due to, e.g., a large change in slope, the smaller `Stepsize=5` was typically used. The IRC calculation was then restarted from the last converged geometry.

The animations of the structures through the IRC paths have been prepared with Jmol, an open-source Java viewer for chemical structures in 3D [12-14]. Atom colours are C: grey, O: red, H: white, B: pink.

File list of the animations.

IRC across TS1a,b,c: `irc_ts1.mp4`

IRC across TS2: `irc_ts2.mp4`

3D rotation to display the reactant complex of TS3 followed by the IRC across TS3: `irc_ts3.mp4`

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