Computational Supporting Information

Computing Organic Stereoselectivity – from Concepts to Quantitative Calculations and Predictions

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2. Derivation of equation 2

The Boltzmann population (i.e. thermal equilibrium) for any species *i* in an equilibrium mixture is given by:

$$p_i = \frac{e^{-\Delta G_i/RT}}{\sum_j e^{-\Delta G_j/RT}} \qquad \text{(S.1)}$$

where the normalization factor sums over all species *j.* To compute the equilibrium ratio of diastereomer A:B, each of which exists as a number of different conformers (the normalization factors cancel):

$$\frac{[A]}{[B]} = \frac{p_{A1}+p_{A2}+p_{A3}+\ldots}{p_{B1}+p_{B2}+p_{B3}+\ldots} = \frac{e^{-\Delta G_{A1}/RT}+e^{-\Delta G_{A2}/RT}+e^{-\Delta G_{A3}/RT}+\ldots}{e^{-\Delta G_{B1}/RT}+e^{-\Delta G_{B2}/RT}+e^{-\Delta G_{B3}/RT}+\ldots} \qquad \text{(S.2)}$$

The most stable conformation of all, in this case A1, is often used as the energy zero. Dividing Eq. S2 by $e^{-\Delta G_{A1}/RT}$ leads to equation 2 in the main text:

$$\frac{[A]}{[B]} = \frac{1+e^{(\Delta G_{A1}-\Delta G_{A2})/RT}+e^{(\Delta G_{A1}-\Delta G_{A3})/RT}+\ldots}{e^{(\Delta G_{A1}-\Delta G_{B1})/RT}+e^{(\Delta G_{A1}-\Delta G_{B2})/RT}+e^{(\Delta G_{A1}-\Delta G_{B3})/RT}+\ldots}$$

2. Cartesian coordinates of computed transition structures used in the text

All molecular graphics were created using the *PyMOL Molecular Graphics System, Version 1.8 Schrödinger, LLC.* 3D animations of each of these structures have also been deposited as Supporting Information

Figure 7. S. Bahmanyar, K. N. Houk, H. J. Martin and B. List, *J. Am. Chem. Soc.*, 2003, **125**, 2475-2479.			
C	1.350917	-1.248179	1.191522
H	-2.498020	-0.778511	-2.848188
H	0.191317	2.382293	-1.047972
C	2.108795	2.261155	-0.033011
H	-2.948406	-2.270007	-2.003207
H	-3.070600	-0.443080	-0.774822
H	-3.302539	-1.066983	0.095818
H	-3.985446	0.075566	-1.068064

H	0.066877	2.026267	0.661883
H	2.157783	3.348619	-0.156085
C	1.634593	-0.542602	-0.552453
H	1.493457	-1.472110	-1.099004
N	-0.706663	-0.142953	-0.794012
H	1.740369	-0.389989	1.770779
C	0.654163	1.803989	-0.234934
C	0.514341	0.341424	-0.598365
O	0.097519	-1.560579	1.378260
C	3.045382	0.041087	-0.693885
H	-2.053934	1.482456	-0.984866
C	-1.953850	0.559281	-0.405860
C	-1.000259	-1.454971	-1.430841
C	-2.058596	0.959856	1.095183
H	2.722992	1.720355	-2.036114
C	2.300528	-2.442865	1.220610
H	4.068912	1.940913	-0.917890
O	-2.860828	1.842206	1.354883
O	-1.332348	0.318127	1.966661
H	-0.679526	-0.554761	1.650112
H	-0.303818	-1.620652	-2.257911
C	-2.453837	-1.301552	-1.885256
H	-0.877894	-2.248486	-0.691354
C	3.050406	1.544131	-1.001264
H	3.592128	-0.507857	-1.469517
H	3.605810	-0.116786	0.238813
H	2.423801	2.049123	0.997124
H	3.322742	-2.195793	0.919332
H	1.914000	-3.240854	0.578592
H	2.329397	-2.826200	2.247630

Figure 8. L. Simón and J. M. Goodman, *J. Am. Chem. Soc.*, 2008, **130**, 8741-8747.

C	1.70400	-1.22900	2.82800
N	0.67800	-1.71200	2.06400
C	0.79800	-2.73800	1.17200
C	2.05900	-3.22200	0.87700
C	2.99000	-1.66500	2.56500
C	3.22400	-2.47500	1.35900
H	3.49000	-1.64600	0.39500
H	-0.23400	-1.15800	2.04900
C	2.22900	-4.42800	0.04700
O	3.54100	-4.65900	-0.23700
O	1.34200	-5.16600	-0.34000
C	4.11600	-1.25400	3.41900
O	5.31800	-1.57400	2.85300
O	4.04500	-0.69700	4.50100
C	3.79200	-5.84400	-1.00700
H	4.87400	-5.87800	-1.14500
H	3.44500	-6.73100	-0.47100
H	3.28000	-5.78900	-1.97000
C	6.46700	-1.23800	3.64400
H	7.32900	-1.56900	3.06400
H	6.51300	-0.16000	3.82000
H	6.43400	-1.75100	4.60900
C	-0.49800	-3.24500	0.60700
H	-0.43300	-3.34600	-0.47800
H	-0.72000	-4.24200	0.99800

H	-1.30700	-2.56000	0.86600
C	1.28100	-0.25900	3.89600
H	1.15400	-0.78300	4.85100
H	2.03700	0.50800	4.06100
H	0.32600	0.19800	3.61900
C	3.40500	-0.61200	-0.63000
P	-1.19800	0.64400	0.45100
O	-1.38600	-0.16600	1.72100
O	0.05900	0.47800	-0.36600
H	1.40000	-0.35400	-0.90000
N	2.23400	-0.84900	-1.28300
O	-2.44200	0.35300	-0.60400
O	-1.38000	2.21300	0.93800
C	0.65600	-1.54000	-2.94200
C	0.27200	-2.33200	-4.02100
C	1.13800	-3.29900	-4.53700
C	2.39100	-3.47400	-3.94800
C	2.79300	-2.69200	-2.86500
C	1.92800	-1.70600	-2.36200
H	-0.01700	-0.79200	-2.53200
H	-0.71000	-2.18700	-4.46200
H	0.83700	-3.91300	-5.38100
H	3.07200	-4.23000	-4.33400
H	3.76000	-2.86100	-2.41000
H	4.15500	-3.03400	1.35600
C	3.34900	0.59500	0.29600
H	3.61100	1.47900	-0.29200
H	2.35100	0.74200	0.71500
H	4.08600	0.50500	1.09700
C	7.22500	-0.68300	-2.63200
C	7.11500	-1.17200	-1.33000
C	5.87600	-1.19300	-0.68700
C	4.72700	-0.73500	-1.34600
C	4.84700	-0.23200	-2.65300
C	6.08700	-0.20700	-3.28900
H	8.19000	-0.66600	-3.13000
H	7.99500	-1.53700	-0.80800
H	5.80300	-1.55800	0.33300
H	3.96700	0.14400	-3.16500
H	6.16400	0.18600	-4.29900
C	-1.72600	3.08600	-0.06600
C	-3.04500	3.07100	-0.57400
C	-1.16100	4.91000	-1.56300
C	-0.78400	4.01900	-0.54700
H	-0.44500	5.63900	-1.92800
C	-4.00500	2.08000	-0.00600
C	-3.66700	0.71400	-0.09300
C	-4.56900	-0.27600	0.33900
C	-5.77800	0.10800	0.93500
H	-6.47200	-0.65400	1.27300
C	-2.77600	5.73200	-3.17700
C	-4.03500	5.66300	-3.77400
C	-4.96600	4.72200	-3.33600
C	-4.65000	3.85400	-2.28900
C	-3.39100	3.92400	-1.65200
C	-2.44100	4.86200	-2.12600
H	-2.06000	6.45900	-3.54300
H	-4.28500	6.33300	-4.58700

H	-5.93600	4.66200	-3.81300
H	-5.39400	3.12700	-1.99300
C	-6.71900	4.16500	1.51800
C	-5.52400	3.81900	0.88100
C	-5.20200	2.46500	0.64900
C	-6.09400	1.46200	1.10800
C	-7.29200	1.82700	1.74300
C	-7.60200	3.17300	1.94200
H	-6.95800	5.20700	1.68500
H	-4.85800	4.61700	0.58300
H	-7.98600	1.07100	2.09100
H	-8.52600	3.44700	2.43500
C	3.26600	4.09900	0.89100
C	3.01300	4.16600	-0.48900
C	1.68700	4.12700	-0.94300
C	0.61500	4.04200	-0.03900
C	0.88600	3.99000	1.33900
C	2.21000	3.99800	1.81000
H	4.28400	4.11400	1.26000
H	1.49300	4.15200	-2.00900
H	0.06400	3.95900	2.04100
C	-3.63600	-4.43900	-0.09000
C	-4.03000	-3.94300	1.16300
C	-4.33900	-2.57800	1.29400
C	-4.24600	-1.71500	0.19000
C	-3.84900	-2.22800	-1.05500
C	-3.54100	-3.59000	-1.20400
H	-3.39300	-5.49000	-0.19600
H	-4.63500	-2.17500	2.25400
H	-3.79300	-1.56100	-1.90600
C	-4.10100	-4.88500	2.33900
C	-3.11000	-4.15900	-2.53300
C	2.52600	3.90400	3.28300
C	4.13400	4.25800	-1.49600
F	3.35100	2.81700	3.50800
F	1.38000	3.75200	4.04600
F	3.17700	5.05500	3.68700
F	4.00500	5.42900	-2.22000
F	4.06500	3.18300	-2.36400
F	5.37600	4.25100	-0.88500
F	-4.50300	-4.23700	3.49400
F	-5.00300	-5.89600	2.06400
F	-2.85400	-5.44100	2.55800
F	-3.98800	-5.15800	-2.91200
F	-3.09000	-3.19200	-3.52200
F	-1.84000	-4.69600	-2.41600

Figure 10. R. N. Straker, Q. Peng, A. Mekareeya, R. S. Paton and E. A. Anderson, *Nat. Commun.*, 2016, **7**, 10109.

Rh	2.0609405	-0.4048841	-0.2119492
P	-0.0579165	0.6628089	-0.4769922
O	-0.9852625	-0.2502441	-1.5959732
O	-1.1571145	0.7110899	0.8193598
N	-0.0660235	2.3043979	-0.8961322
C	-3.2224645	-0.3585341	-0.7425522
C	-2.3394065	-0.0267891	-1.7492572
C	-2.7667795	0.4926269	-2.9898692

H	-2.0231335	0.6697659	-3.7600422
C	-4.0952175	0.7435349	-3.1941892
H	-4.4392355	1.1333969	-4.1480782
C	-5.0395685	0.5302819	-2.1565342
C	-6.4089775	0.8581769	-2.3332652
H	-6.7284945	1.2630269	-3.2897332
C	-7.3104315	0.6797499	-1.3173052
H	-8.3553945	0.9350119	-1.4608762
C	-6.8750205	0.1702979	-0.0725752
H	-7.5894115	0.0499159	0.7358848
C	-5.5608255	-0.1675621	0.1253628
H	-5.2411935	-0.5508381	1.0882898
C	-4.6040835	-0.0132031	-0.9138192
C	-2.7180195	-1.0640761	0.4663198
C	-1.6929855	-0.5123031	1.2003348
C	-1.1699765	-1.1191291	2.3601768
H	-0.3989385	-0.6037581	2.9215298
C	-1.6642955	-2.3256441	2.7686518
H	-1.2797745	-2.8016321	3.6662388
C	-2.6849535	-2.9745541	2.0286838
C	-3.1794905	-4.2420021	2.4306988
H	-2.7707295	-4.6984101	3.3282138
C	-4.1513345	-4.8798921	1.7062948
H	-4.5299355	-5.8456181	2.0263778
C	-4.6570575	-4.2795241	0.5312018
H	-5.4142185	-4.7947501	-0.0519502
C	-4.2000565	-3.0540541	0.1178908
H	-4.5932375	-2.6146811	-0.7913922
C	-3.2154715	-2.3506991	0.8635488
C	-1.2262625	3.2139549	-0.6974292
H	-1.9927345	2.6033009	-0.2156152
C	-1.8158255	3.7396719	-2.0057452
H	-2.1850485	2.9132819	-2.6155062
H	-1.0989315	4.3137439	-2.6007772
H	-2.6575385	4.4002999	-1.7778302
C	-0.8385505	4.3129909	0.2823178
C	-0.3107435	5.5380329	-0.1330102
H	-0.2200505	5.7687869	-1.1906462
C	0.0980065	6.4898399	0.7997128
H	0.5092115	7.4349689	0.4583438
C	-0.0333705	6.2354689	2.1614788
H	0.2770105	6.9797469	2.8881438
C	-0.5853845	5.0281829	2.5856468
H	-0.7121305	4.8293049	3.6456948
C	-0.9818925	4.0770959	1.6514548
H	-1.4051725	3.1330109	1.9840548
C	1.0618855	2.7536969	-1.7405242
H	0.9251405	3.8340579	-1.8319802
C	0.9986385	2.1560389	-3.1494452
H	0.0417265	2.4067229	-3.6134572
H	1.0794525	1.0633059	-3.1352742
H	1.8032535	2.5503909	-3.7776092
C	2.4168325	2.5779069	-1.0563392
C	3.3464925	1.6038489	-1.4532022
H	3.1412615	0.9377199	-2.2878962
C	4.6317885	1.5728899	-0.8906882
H	5.3419185	0.8239429	-1.2297582
C	4.9965305	2.5121179	0.0633738

H	5.9988295	2.5062369	0.4804158
C	4.0717745	3.4800549	0.4682918
H	4.3549915	4.2250019	1.2059828
C	2.7938535	3.5020509	-0.0723542
H	2.0821135	4.2605699	0.2433568
C	2.9839425	-2.3036851	-0.1776382
C	1.6831135	-2.3618361	-0.2052612
C	0.6154625	-3.3374391	-0.2429982
C	0.6509145	-4.4098371	0.6621498
C	-0.4120465	-3.2615761	-1.1895622
C	-0.3300975	-5.3902431	0.6163678
H	1.4490275	-4.4640311	1.3968948
C	-1.3781825	-4.2582191	-1.2405022
H	-0.4411025	-2.4277891	-1.8802212
C	-1.3416335	-5.3188001	-0.3394892
H	-0.3059535	-6.2126351	1.3242008
H	-2.1692445	-4.2011761	-1.9805862
H	-2.1091245	-6.0845391	-0.3733512
N	4.1403075	-3.0146551	-0.3736242
C	4.9652995	-3.0391231	0.8503018
C	4.2055965	-2.2336771	1.9107808
H	5.9402945	-2.5861531	0.6408718
H	5.1121605	-4.0770921	1.1567688
H	3.4151825	-2.8377741	2.3662018
H	4.8927275	-1.9244941	2.7066368
C	3.6251575	-0.9786141	1.2835388
C	2.4430415	-0.3354601	1.8272218
H	4.4087515	-0.2951871	0.9506888
H	1.7512705	-0.9913351	2.3590888
C	2.5550365	1.0367379	2.3634768
C	1.3429365	1.8530889	2.7387578
C	2.1958605	1.2817359	3.8221758
H	3.4001955	1.5985049	1.9830788
H	0.3636125	1.4239979	2.5614718
H	1.4011495	2.9172429	2.5371878
H	2.8430065	1.9431709	4.3890208
H	1.8083315	0.4386349	4.3878948
S	5.0396835	-2.2628121	-1.8384072
O	3.9925365	-1.4759811	-2.6251972
O	6.2998985	-1.5673561	-1.3188162
C	5.4882865	-3.7805221	-2.7628722
H	6.0108645	-3.4541371	-3.6626172
H	6.1316855	-4.3701541	-2.1101472
H	4.5504655	-4.2863131	-2.9892442

Figure 12. R. S. Paton *Org. Biomol. Chem*. **2014**, *12,* 1717-1720.

C	-2.47193	-0.77229	-0.13177
C	-1.98092	-1.28927	-1.49916
H	-2.79614	-1.54978	-2.17950
B	-0.56667	0.54134	-0.68729
O	-1.3577	-0.03211	0.35806
N	-1.19728	-0.13191	-2.04341
H	-1.81912	0.57342	-2.44699
C	-0.26227	-0.67742	-3.07848
H	-0.75253	-0.60248	-4.05137
H	0.64736	-0.07624	-3.09324
C	-0.93239	-2.40269	-1.45310

H	-0.36975	-2.33232	-0.51826
C	-0.01651	-2.14285	-2.66649
H	1.03408	-2.30634	-2.41378
H	-0.2651	-2.80632	-3.49764
H	-1.40722	-3.38491	-1.47686
C	-2.79304	-1.93863	0.78815
C	-3.95127	-2.68317	0.55008
C	-1.9401	-2.30724	1.82614
C	-4.24688	-3.79219	1.33364
H	-4.6336	-2.38115	-0.24160
C	-2.24459	-3.41388	2.61849
H	-1.04498	-1.72092	2.01227
C	-3.39277	-4.15966	2.37202
H	-5.14898	-4.36385	1.14043
H	-1.58231	-3.69256	3.43247
H	-3.62726	-5.02058	2.98972
C	-3.66799	0.18104	-0.23387
C	-4.10953	0.7666	0.95894
C	-4.30213	0.53067	-1.42471
C	-5.14621	1.68866	0.95684
H	-3.62586	0.48567	1.89132
C	-5.34618	1.45869	-1.43000
H	-4.01784	0.07659	-2.37124
C	-5.7669	2.04154	-0.24283
H	-5.47972	2.12896	1.89140
H	-5.83045	1.71583	-2.36664
H	-6.58113	2.75895	-0.24608
O	4.26873	-1.41742	1.96599
C	3.29882	-0.78783	1.65361
C	1.28498	0.38754	1.70846
C	1.55346	-0.07738	0.39016
H	0.31057	0.74158	2.01564
N	2.78033	-0.67606	0.33126
O	0.84513	-0.04022	-0.67039
C	3.34703	-1.2639	-0.83988
C	3.42471	-0.50717	-2.00853
C	3.79356	-2.58249	-0.80410
C	3.93561	-1.08837	-3.16360
H	3.08368	0.52389	-2.00271
C	4.31847	-3.14739	-1.96341
H	3.73914	-3.15022	0.11785
C	4.38293	-2.40854	-3.14204
H	3.99671	-0.50585	-4.07724
H	4.6742	-4.17204	-1.94256
H	4.78909	-2.85739	-4.04242
C	-0.4952	2.12882	-0.79651
C	-1.33754	2.94027	-0.02805
C	0.42364	2.7581	-1.65004
C	-1.25608	4.33127	-0.09537
H	-2.06078	2.47177	0.63460
C	0.5119	4.14543	-1.72684
H	1.09716	2.15278	-2.25777
C	-0.32827	4.93548	-0.94117
H	-1.91609	4.94413	0.51124
H	1.23044	4.61259	-2.39408
H	-0.26243	6.01786	-0.99490
C	2.3793	0.0392	2.51821
C	3.11889	2.47522	0.47800

C	4.07149	1.8192	1.28048
C	3.57701	1.7057	2.59205
C	2.44347	2.70038	2.70533
C	2.05379	2.85648	1.27077
H	1.63335	2.44625	3.39006
H	2.87186	3.65799	3.04084
H	4.21286	1.43516	3.42908
H	1.16503	3.37807	0.93029
H	5.0037	1.38923	0.92867
H	3.17888	2.61206	-0.59549
C	2.30516	-0.30247	3.98346
H	1.67084	-1.18392	4.11948
H	3.29801	-0.53757	4.37281
H	1.87415	0.51584	4.56516