

SUPPORTING INFORMATION FOR

Quantum Tunneling in *n*-Alkyl Radicals Isomerization

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Table S1: Optimized geometries (Cartesian coordinates) at the B3LYP/6-311G(2d,d,p) level of theory.

1-pentyl

6	1.359543	0.483813	0.021480
6	2.599083	-0.340884	-0.018797
1	3.545518	0.087198	-0.325907
1	2.608679	-1.345032	0.389920
6	0.061399	-0.336285	-0.036094
6	-1.207096	0.520232	0.036465
6	-2.496401	-0.303938	-0.020671
1	-2.557860	-0.877586	-0.950723
1	-3.382084	0.334907	0.034254
1	-2.548005	-1.015279	0.809546
1	-1.191215	1.110868	0.960619
1	-1.200612	1.244726	-0.786926
1	0.058991	-1.059433	0.789424
1	0.051675	-0.927180	-0.959818
1	1.371653	1.214995	-0.797726
1	1.344089	1.094191	0.943042

2-pentyl

6	-2.537325	-0.288918	-0.012553
6	-1.244189	0.526666	-0.086369
6	0.020425	-0.322473	0.106550
6	1.293613	0.454351	0.052834
6	2.614884	-0.223388	-0.075768
1	3.413581	0.481053	-0.321828
1	2.913324	-0.731037	0.857625
1	2.596368	-1.000137	-0.850248
1	1.269535	1.502163	0.338356
1	-0.058199	-0.854687	1.073558
1	0.044989	-1.122297	-0.648688
1	-1.184590	1.038883	-1.053101
1	-1.263894	1.314238	0.676158
1	-2.561989	-1.063084	-0.785960
1	-3.417217	0.345191	-0.150797
1	-2.636356	-0.787713	0.956765

TS 1-pentyl ⇌ 2-pentyl (5ps)

6	-0.122478	-1.003783	-0.178094
6	0.807840	0.022094	0.463069
1	0.836637	-0.046941	1.553866
6	2.153707	0.291659	-0.161921
6	-1.552521	-0.452597	0.049031
6	-1.424207	1.055704	-0.113354
1	-1.392875	1.422328	-1.139555
1	-2.002487	1.698270	0.546475
1	-2.282507	-0.903004	-0.631137
1	-1.878237	-0.687095	1.067935
1	0.082291	-1.052524	-1.254431
1	0.007877	-2.016329	0.218495
1	-0.084161	1.033888	0.272792
1	2.817116	-0.581583	-0.083661
1	2.058075	0.526287	-1.227003
1	2.664231	1.128245	0.323842

1-hexyl

6	0.593824	-0.366175	0.018188
6	-0.734692	0.394818	-0.036417
1	0.630014	-0.968336	0.935562
1	0.637615	-1.080069	-0.814712
6	-1.968338	-0.519852	0.018534
1	-0.781405	1.106194	0.797791
1	-0.776138	0.995316	-0.952886
6	-3.265210	0.212193	-0.006119
1	-1.931392	-1.241036	-0.808737
1	-1.902982	-1.137365	0.933089
1	-4.180243	-0.281478	-0.309981
1	-3.344910	1.209719	0.411072
6	1.825403	0.545034	-0.035368
1	1.788853	1.146249	-0.951884
1	1.782382	1.257984	0.796888
6	3.149521	-0.222333	0.018727
1	4.006526	0.455475	-0.022966
1	3.231692	-0.804895	0.941706
1	3.236938	-0.919872	-0.820214

2-hexyl

6	0.700161	-0.391122	0.097223
6	-0.626813	0.372529	-0.012544
1	-0.684912	1.108737	0.799261
1	-0.632957	0.947145	-0.946699
6	-1.861526	-0.533513	0.037179
1	-1.800346	-1.270796	-0.772556
6	-3.181036	0.235506	-0.073343
1	-3.288547	0.956241	0.743382
1	-3.236320	0.792623	-1.013820
1	-4.041215	-0.438560	-0.036095
1	-1.850347	-1.107756	0.971675
1	0.761483	-1.139997	-0.706720
1	0.689253	-0.985322	1.030467
6	1.912168	0.479222	0.060909
6	3.277044	-0.094827	-0.109956
1	4.017221	0.673609	-0.347537
1	3.629372	-0.605766	0.802648
1	3.301140	-0.847964	-0.907217
1	1.816190	1.511041	0.386402

3-hexyl

6	-3.186317	0.330649	0.142248
6	-1.937607	-0.545201	-0.015392
6	-0.672483	0.228746	-0.185300
6	0.667506	-0.421969	-0.093346
6	1.838337	0.564543	0.027612
6	3.203249	-0.124054	0.101978
1	-3.323803	0.976882	-0.729896
1	-3.104561	0.973819	1.022776
1	-4.087893	-0.277913	0.250860
1	-2.083811	-1.220912	-0.877969
1	-1.843689	-1.216893	0.849693
1	-0.732175	1.226932	-0.613375
1	0.683733	-1.117159	0.759030
1	0.839183	-1.062231	-0.979256
1	1.818239	1.247434	-0.829878
1	1.689005	1.186516	0.917145
1	3.264716	-0.788676	0.969506

1 4.013886 0.604891 0.185348
1 3.391063 -0.728974 -0.790784

TS 1-hexyl ⇌ 2-hexyl (6ps)

6 0.343509 -1.157680 -0.121286
6 -1.158892 -1.068005 0.202606
6 -1.777886 0.219572 -0.379789
6 -1.086566 1.462154 0.149237
1 -1.048722 2.321672 -0.518184
1 -1.355267 1.743697 1.168042
1 -1.691405 0.185215 -1.472157
1 -2.853153 0.239935 -0.157327
1 -1.681755 -1.945021 -0.191471
1 -1.299404 -1.081182 1.290981
1 0.750616 -2.105772 0.257334
1 0.468513 -1.185411 -1.211772
6 1.116144 0.023676 0.443870
1 1.208182 -0.021121 1.532795
6 2.405875 0.409591 -0.245175
1 3.151252 -0.396175 -0.186883
1 2.242587 0.618124 -1.307739
1 2.854543 1.298915 0.206178
1 0.200908 0.991268 0.293421

TS 1-hexyl ⇌ 3-hexyl (5ps)

6 -0.945532 -1.073422 -0.083760
6 0.272384 -0.276881 0.374877
1 0.380520 -0.241468 1.463437
6 1.586176 -0.437862 -0.352327
1 1.941635 -1.474295 -0.238433
1 1.423947 -0.301098 -1.428784
6 2.678234 0.521849 0.132375
1 2.374796 1.563460 -0.005936
1 2.886082 0.375925 1.196675
6 -2.156359 -0.135300 0.150576
6 -1.651963 1.257163 -0.201415
1 -1.611933 1.493759 -1.264873
1 -1.984588 2.096483 0.404862
1 -3.033968 -0.439574 -0.428794
1 -2.444339 -0.166462 1.206669
1 -0.853433 -1.288667 -1.155141
1 -1.052791 -2.035556 0.428030
1 -0.336693 0.915290 0.113543
1 3.613122 0.368922 -0.413207

1-heptyl

6 2.642328 0.458975 0.012132
6 3.887841 -0.357413 -0.011164
1 4.831606 0.071325 -0.325579
1 3.904081 -1.353530 0.416552
6 1.349924 -0.371488 -0.030945
6 0.075788 0.478350 0.019912
6 -1.214580 -0.347838 -0.021103
1 -1.223585 -0.960673 -0.931825
1 -1.219327 -1.054203 0.819209
1 0.084867 1.090458 0.931197
1 0.078877 1.185147 -0.819983
1 1.351450 -1.076712 0.809728
1 1.347720 -0.981851 -0.941771
1 2.650092 1.174319 -0.820959

1	2.621490	1.086924	0.921662
6	-2.490788	0.500144	0.027547
1	-2.486741	1.205977	-0.812082
1	-2.482462	1.111979	0.938000
6	-3.774126	-0.334297	-0.014384
1	-3.822764	-1.027105	0.831791
1	-4.665048	0.298898	0.023569
1	-3.828580	-0.929562	-0.931481

2-heptyl

6	1.322114	-0.362663	0.099666
6	0.046465	0.483800	-0.014353
1	0.037922	1.227313	0.792578
1	0.077068	1.051135	-0.952317
6	-1.243458	-0.340826	0.042551
1	-1.233763	-1.085228	-0.764341
6	-2.518161	0.503457	-0.068349
6	-3.802489	-0.328800	-0.013560
1	-3.875082	-0.882351	0.927912
1	-4.691922	0.301777	-0.096941
1	-3.835507	-1.058760	-0.828476
1	-2.529829	1.246137	0.738574
1	-2.491977	1.073619	-1.004878
1	-1.268994	-0.911067	0.980436
1	1.333977	-1.120443	-0.698088
1	1.275194	-0.947182	1.037860
6	2.587010	0.428388	0.054475
6	3.912668	-0.232877	-0.109812
1	4.699994	0.484606	-0.355081
1	4.232076	-0.755441	0.808309
1	3.888958	-0.994353	-0.899114
1	2.556991	1.467365	0.369858

3-heptyl

6	-0.015092	0.571483	-0.082534
6	-1.299051	-0.180565	-0.199235
6	-2.620493	0.476506	0.025246
6	-3.790768	-0.507195	0.144606
1	-3.645771	-1.187433	0.988359
1	-3.884174	-1.115098	-0.760302
1	-4.738301	0.017516	0.292423
1	-2.570056	1.105168	0.925630
1	-2.833321	1.184160	-0.796873
1	-1.283866	-1.156960	-0.678250
1	0.082911	1.284854	-0.922394
1	-0.038135	1.204012	0.817281
6	1.233716	-0.320986	-0.051003
1	1.154580	-1.017455	0.792516
1	1.254515	-0.940086	-0.956911
6	2.546174	0.462442	0.056071
1	2.619449	1.160959	-0.786486
1	2.524255	1.081002	0.961596
6	3.785698	-0.436263	0.082705
1	4.704413	0.151356	0.162057
1	3.756954	-1.124147	0.933539
1	3.855439	-1.040381	-0.827319

4-heptyl

6	1.304610	-0.392149	-0.134895
6	0.000002	0.327586	-0.221414

6	-1.304630	-0.392142	-0.135104
1	-1.471849	-0.985346	-1.054021
1	-1.262274	-1.137789	0.672621
6	-2.517182	0.525835	0.078010
1	-2.369858	1.102249	0.998061
1	-2.557794	1.257125	-0.737839
6	-3.844140	-0.233542	0.151431
1	-4.685890	0.447684	0.302390
1	-4.031520	-0.794116	-0.769905
1	-3.844731	-0.949798	0.979144
1	-0.000013	1.352713	-0.585079
6	2.517213	0.525857	0.077790
6	3.844134	-0.233557	0.151486
1	4.031455	-0.794529	-0.769620
1	3.844718	-0.949465	0.979500
1	4.685925	0.447689	0.302128
1	2.557831	1.256804	-0.738364
1	2.369945	1.102659	0.997607
1	1.262269	-1.137473	0.673131
1	1.471746	-0.985736	-1.053581

TS 1-heptyl ⇌ 2-heptyl (7ps)

6	0.713886	-1.500194	-0.215609
6	1.798695	-0.547901	0.324015
6	1.809412	0.878359	-0.259135
6	0.641372	1.737631	0.175112
1	0.550433	1.875842	1.254032
1	0.518372	2.675012	-0.367358
1	2.752719	1.363036	0.030816
1	1.833524	0.815798	-1.354491
1	1.714289	-0.488864	1.417416
1	2.774475	-1.004045	0.122476
1	0.767177	-1.521810	-1.312284
1	0.964570	-2.513926	0.116178
6	-0.734821	-1.202709	0.215193
1	-1.358950	-2.076034	-0.026180
1	-0.770848	-1.106942	1.309003
6	-1.343930	0.034790	-0.416868
1	-1.313846	-0.001282	-1.510347
6	-2.688773	0.472844	0.121936
1	-3.035242	1.393073	-0.356662
1	-3.458320	-0.293194	-0.046311
1	-2.644685	0.652026	1.201430
1	-0.468711	0.994389	-0.145581

TS 1-heptyl ⇌ 3-heptyl (6ps)

6	-0.511733	-1.325356	-0.090813
6	-1.905167	-0.789817	0.286374
6	-2.162760	0.591777	-0.348578
6	-1.117431	1.606293	0.075472
1	-0.877352	2.389022	-0.642519
1	-1.235618	1.997847	1.086479
1	-2.151876	0.482944	-1.439447
1	-3.173155	0.931513	-0.084200
1	-2.677972	-1.496683	-0.031528
1	-1.982943	-0.710084	1.378244
1	-0.372262	-2.329606	0.332994
1	-0.463355	-1.444452	-1.181224
6	0.598333	-0.391239	0.363941
1	0.743648	-0.410324	1.448948

6	1.903041	-0.424000	-0.404115
1	2.321631	-1.442361	-0.370553
1	1.704284	-0.224579	-1.464858
6	2.949227	0.565682	0.118773
1	3.877531	0.504802	-0.455681
1	2.583553	1.594742	0.056839
1	3.192565	0.363560	1.166424
1	-0.009746	0.793628	0.193763

TS 1-heptyl ⇌ 4-heptyl (5ps)

6	-1.570317	-1.054682	-0.138754
6	-0.361042	-0.325797	0.440296
1	-0.333916	-0.336869	1.534231
6	0.995643	-0.512275	-0.195780
1	1.306920	-1.565252	-0.095082
1	0.919094	-0.332400	-1.276411
6	2.090865	0.384973	0.395807
1	1.790230	1.433504	0.289102
1	2.164351	0.197370	1.473692
6	3.460836	0.173785	-0.254426
1	4.217774	0.827212	0.187809
1	3.801803	-0.859208	-0.132840
1	3.426151	0.385498	-1.327735
6	-2.759439	-0.077772	0.041856
6	-2.177895	1.305491	-0.214010
1	-2.048013	1.580669	-1.260886
1	-2.524253	2.133864	0.399607
1	-3.600633	-0.324139	-0.614009
1	-3.128936	-0.137062	1.071037
1	-1.405761	-1.234615	-1.207884
1	-1.752701	-2.029702	0.325248
1	-0.904010	0.898800	0.184185

TS 2-heptyl ⇌ 3-heptyl (5ss)

6	-0.153062	1.571749	0.023376
6	-1.601786	1.030061	0.091685
6	-1.526877	-0.391070	-0.455832
6	-2.426141	-1.454410	0.122573
1	-3.483552	-1.263150	-0.111263
1	-2.343158	-1.495070	1.213658
1	-2.184486	-2.446030	-0.271117
1	-1.444249	-0.429517	-1.545373
1	-1.931468	0.997142	1.137121
1	-2.312390	1.666738	-0.446520
1	0.070120	1.890932	-1.001730
1	-0.002871	2.443913	0.668572
6	0.737021	0.388735	0.388330
1	0.759619	0.178484	1.462050
6	2.080383	0.231169	-0.282807
1	1.951291	0.290659	-1.370886
1	2.726534	1.083350	-0.017466
6	2.799263	-1.072302	0.081804
1	3.769805	-1.144721	-0.416424
1	2.973201	-1.136924	1.160312
1	2.205482	-1.943319	-0.210261
1	-0.206680	-0.516078	-0.065445

1-octyl

6	4.543195	0.252752	-0.003076
6	3.265897	-0.513242	0.011515
6	2.008439	0.369245	-0.028546
6	0.700748	-0.428194	0.014382
6	-0.554390	0.450978	-0.024075
6	-1.863752	-0.344960	0.015550
6	-3.119464	0.533557	-0.024128
1	0.676650	-1.129213	-0.829960
1	0.682602	-1.045729	0.921817
1	2.033040	0.985008	-0.935412
1	2.036766	1.068412	0.816723
1	3.217689	-1.145957	0.916685
1	3.246927	-1.222467	-0.826593
1	4.598400	1.243892	0.432905
1	5.469669	-0.211119	-0.319033
1	-0.531287	1.151107	0.820980
1	-0.534673	1.069495	-0.930634
1	-1.887443	-1.045697	-0.829203
1	-1.884817	-0.963358	0.922421
6	-4.422542	-0.269867	0.016548
1	-3.095996	1.233949	0.819532
1	-3.098875	1.150397	-0.930794
1	-5.297704	0.384945	-0.015160
1	-4.490518	-0.956205	-0.833373
1	-4.489220	-0.869075	0.930086

2-octyl

6	3.144669	-.527712	-.015611
6	1.888471	.350098	.024718
6	.580259	-.444675	-.053056
6	-.675022	.432959	-.009335
6	1.984040	-.364836	-.090924
6	3.216574	.476193	-.056598
6	4.565338	-.128255	.136056
1	-.643539	1.153583	-.836212
1	-.675105	1.026099	.913011
1	.546357	-1.165541	.774115
1	3.137894	-1.123999	-.936119
6	4.447036	.273830	.063354
1	3.108088	-1.246836	.811635
1	1.925081	1.069910	-.803344
1	1.895460	.947514	.945667
1	.573599	-1.040750	-.974906
1	2.018453	-1.100482	.726691
1	1.968420	-.975194	-1.013583
1	5.321743	.625376	.369969
1	4.913829	-.660768	-.765629
1	4.563437	-.870113	.944178
1	3.149071	1.504772	-.399093
1	5.322438	-.380673	.031728
1	4.528965	.978349	-.770312
1	4.498945	.853143	.990578

3-octyl

6	4.452979	.430324	.185186
6	3.255396	-.514268	.027242
6	1.956483	.187586	-.193112
6	.649986	-.529557	-.112028
6	-.572872	.398054	-.069845

6	-1.908338	-.349632	-.002803
6	-3.129089	.576741	.034276
1	4.318564	1.092333	1.045031
1	4.575211	1.058518	-.702265
1	5.382596	-.126459	.329420
1	3.176496	-1.164805	.909873
1	3.456236	-1.205881	-.811378
1	1.975190	1.176379	-.645882
1	.541962	-1.216161	-.972710
1	.643744	-1.187253	.769776
1	-.483907	1.066778	.794702
1	-.562620	1.043304	-.957324
1	-1.991790	-1.021755	-.866971
1	-1.919026	-.995378	.885002
6	-4.460340	-.176964	.101334
1	-3.045894	1.247856	.897714
1	-3.118721	1.221639	-.852773
1	-5.309151	.511875	.127644
1	-4.589608	-.829856	-.767621
1	-4.514517	-.804833	.996259

4-octyl

6	-3.190943	-.484309	.080538
6	-1.895361	.323514	-.048047
6	-.632644	-.546016	-.127795
6	.634637	.230513	-.265419
6	1.973448	-.406588	-.094832
6	3.130365	.592816	.052510
6	4.495927	-.081973	.202915
1	-.740814	-1.246957	-.976849
1	-.574498	-1.193084	.760030
1	-1.805654	1.007428	.804668
1	-1.950858	.956855	-.942595
6	-4.444760	.391793	.152533
1	-3.273948	-1.171488	-.770407
1	-3.135245	-1.115657	.975725
1	.588433	1.216149	-.722982
1	4.727177	-.705950	-.666226
1	4.524159	-.725694	1.087759
1	5.296645	.655596	.304334
1	3.142359	1.254361	-.821735
1	2.937391	1.235037	.918967
1	1.955666	-1.078468	.775988
1	2.190656	-1.068824	-.954169
1	-5.350682	-.213169	.247275
1	-4.405720	1.068045	1.012261
1	-4.549082	1.007330	-.746471

TS 1-octyl ⇌ 2-octyl (8ps)

6	1.646050	-1.177592	-0.245750
6	2.118511	0.220698	0.201110
6	1.421972	1.445538	-0.428090
6	0.195622	1.941769	0.304360
1	0.363742	2.176449	1.357280
1	-0.350177	2.740410	-0.199700
1	2.153592	2.266158	-0.472170
1	1.173102	1.225788	-1.473740
1	2.065021	0.293768	1.295050
1	3.183891	0.281307	-0.046760
1	1.602530	-1.203512	-1.342770

1	2.442449	-1.878233	0.031020
6	0.333669	-1.758561	0.318690
1	0.379948	-2.840941	0.157420
1	0.311849	-1.624331	1.407810
6	-0.991990	-1.252200	-0.287930
1	-1.720181	-2.077579	-0.263760
6	-1.617839	-0.058259	0.405310
6	-2.881969	0.486182	-0.227000
1	-2.713529	0.770802	-1.271120
1	-3.688060	-0.260038	-0.221900
1	-3.250878	1.367942	0.304470
1	-1.723080	-0.219859	1.482730
1	-0.727479	0.925000	0.365170
1	-0.846890	-1.028580	-1.353230

TS 1-octyl ⇌ 3-octyl (7ps)

6	1.560234	-1.319148	-.312677
6	2.365317	-.120088	.224419
6	1.920937	1.273474	-.258917
6	.590688	1.731954	.299352
1	.543470	1.779074	1.388922
1	.168354	2.623135	-.164915
1	2.703390	1.997926	.008949
1	1.879723	1.274320	-1.355535
1	2.353393	-.141170	1.322395
1	3.412005	-.262295	-.067141
1	1.534085	-1.272719	-1.409536
1	2.114983	-2.231088	-.065050
6	.124240	-1.475896	.221572
1	-.236831	-2.482323	-.036876
1	.145007	-1.441578	1.319263
6	-.862680	-.445213	-.294842
1	-.908388	-.425247	-1.389284
6	-2.235857	-.439747	.347009
6	-3.183319	.615083	-.233602
1	-2.783063	1.623790	-.097629
1	-3.333814	.460389	-1.306519
1	-4.164080	.577474	.248182
1	-2.692869	-1.435512	.236440
1	-2.129763	-.284685	1.428363
1	-.282967	.717990	-.013919

TS 1-octyl ⇌ 4-octyl (6ps)

6	-1.138736	-1.324965	-.118045
6	-2.521038	-.709006	.167502
6	-2.635041	.707609	-.432317
6	-1.568196	1.634910	.117962
1	-1.217549	2.424341	-.545110
1	-1.747100	1.997645	1.130784
1	-2.536828	.634958	-1.521828
1	-3.641088	1.104177	-.240542
1	-3.308942	-1.351178	-.238389
1	-2.683381	-.660163	1.251854
1	-1.098995	-2.348232	.280399
1	-1.011624	-1.415157	-1.204744
6	-.009808	-.481215	.453374
1	.056411	-.552966	1.543690
6	1.341090	-.562010	-.225687
1	1.703963	-1.602917	-.202698
1	1.228190	-.315549	-1.290183

6	2.407224	.348238	.397128
6	3.767113	.251011	-.299537
1	4.504084	.909166	.168777
1	4.160608	-.769653	-.259626
1	3.692506	.534334	-1.354197
1	2.053620	1.385328	.369367
1	2.520356	.093743	1.457778
1	-.529878	.744693	.292384

TS 1-octyl ⇌ 4-octyl (5ps)

6	-2.263272	-.989666	-.059490
6	-.969054	-.358317	.445791
1	-.911371	-.306857	1.537369
6	.342088	-.721859	-.209505
1	.550506	-1.791936	-.045575
1	.247970	-.605438	-1.297318
6	1.537274	.098974	.292067
1	1.334079	1.164809	.129858
1	1.633838	-.030206	1.377741
6	2.863190	-.273212	-.380607
1	3.063762	-1.339304	-.218324
1	2.765193	-.145058	-1.465513
6	-3.339104	.116020	.085734
6	-2.624672	1.412804	-.268265
1	-2.497033	1.610190	-1.332835
1	-2.865920	2.307936	.300287
1	-4.219422	-.078991	-.535115
1	-3.683728	.157318	1.124372
1	-2.148560	-1.249684	-1.118663
1	-2.532045	-1.910604	.468524
1	-1.389043	.899042	.126109
6	4.050412	.551709	.124233
1	4.198538	.414786	1.200038
1	4.978844	.265080	-.377314
1	3.893221	1.620203	-.053384

TS 2-octyl ⇌ 3-octyl (6ss)

6	.908663	-.359518	.681155
6	.120605	-1.662317	.629249
6	-.956822	-1.659182	-.476812
6	-1.932187	-.481810	-.300630
6	-1.215419	.856348	-.357552
6	-1.858594	2.026918	.349978
1	1.160853	-.033584	1.693052
6	2.070174	-.218224	-.283117
1	-.374921	-1.830698	1.592112
1	.796690	-2.516036	.477455
1	-1.503831	-2.607056	-.461730
1	-.479220	-1.592756	-1.461953
1	-2.722031	-.535109	-1.063500
1	-2.437492	-.582609	.669050
1	-.863202	1.100901	-1.363669
1	-2.834674	2.278982	-.088927
1	-2.032260	1.805650	1.408473
1	-1.237247	2.925133	.293083
1	-.052876	.510120	.263405
6	2.743741	1.157070	-.232063
1	2.818814	-.995306	-.063392
1	1.730685	-.420438	-1.306595
1	3.587882	1.214362	-.924733

1	2.039539	1.951518	-.495664
1	3.122320	1.371220	.772279

TS 2-octyl ⇌ 4-octyl (5ss)

6	.931770	-1.613349	-.031573
6	2.288993	-.867615	-.014480
6	1.972594	.553043	-.468795
6	2.746765	1.707421	.115813
1	3.802087	1.687036	-.192884
1	2.734012	1.681520	1.210394
1	2.337700	2.670547	-.203242
1	1.809586	.633591	-1.546866
1	2.678841	-.841038	1.010293
1	3.046788	-1.363206	-.631001
1	.689146	-1.907737	-1.059634
1	.952390	-2.530979	.566039
6	-.093350	-.595660	.457398
1	-.075406	-.450256	1.541798
6	-1.485249	-.596134	-.127493
1	-1.419256	-.582309	-1.223770
1	-1.993690	-1.542143	.123322
6	-2.358225	.573467	.346336
1	-2.429935	.546681	1.440235
1	-1.857244	1.516020	.097428
1	.679055	.459952	.008134
6	-3.764553	.563092	-.258765
1	-4.300932	-.355198	.000531
1	-4.360012	1.407300	.099474
1	-3.725597	.624635	-1.350898

Table S2: Characteristics of hindered potentials of *n*-pentyl radicals and *5ps* transition states of 1-pentyl and 1-hexyl. Relaxed scans performed at the B3LYP/cbsb7 level of theory and barrier heights computed at the CBS-QB3 level of theory.

Rotors	Symmetry	Number of minima	Hindrance (kcal.mol ⁻¹)	Rotation
1-pentyl				
	2	2	0.2	Free
	1	2	5.2	Hindered
	1	2	5.9	Hindered
	3	3	3.1	Hindered
2-pentyl				
	3	3	0.3	Hindered
	1	2	1.6	Hindered
	1	2	5.3	Hindered
3-pentyl				
	1	2	6.3	Hindered
	3	3	2.8	Hindered
TS <i>5ps</i> pentyl¹				
	3	3	2.0	Hindered
TS <i>5ps</i> hexyl¹				
	1	2	3.9	Hindered
	3	3	2.8	Hindered

¹ Vibrational modes of the cyclic part of the molecular structure were described within the HO approximation

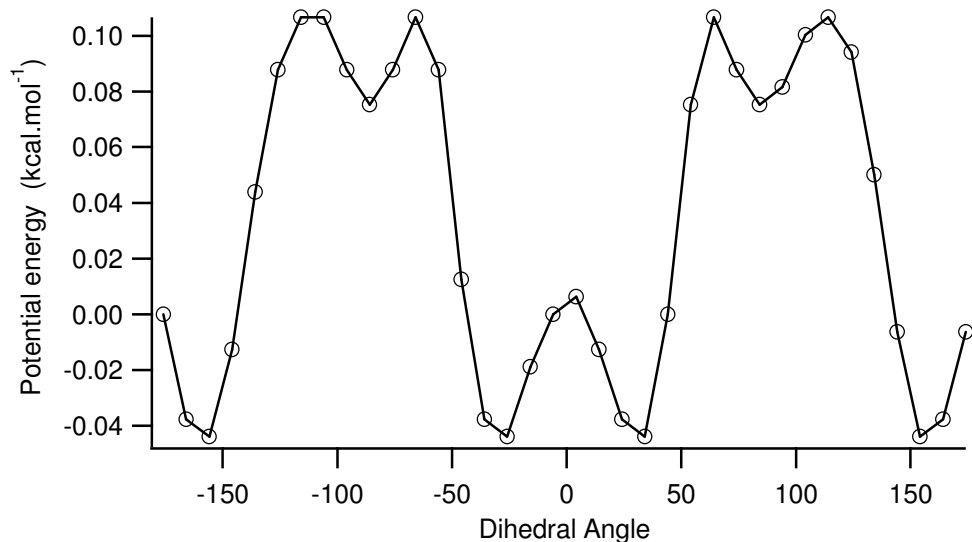


Figure S1: Potential of **•CH₂-CH₂-C₃H₇** internal rotor of 1-pentyl

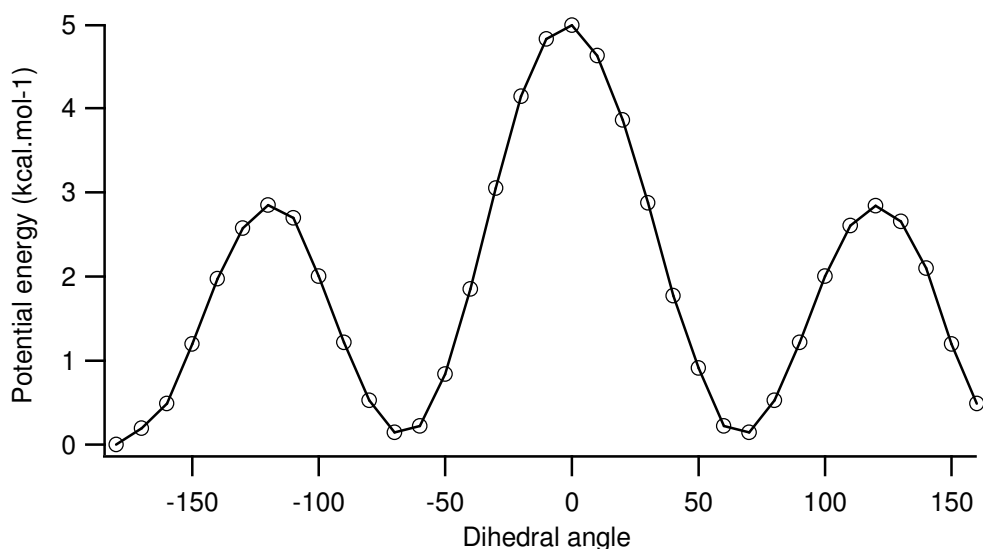


Figure S2: Potential of **•CH₂-CH₂-CH₂-C₂H₅** internal rotor of 1-pentyl

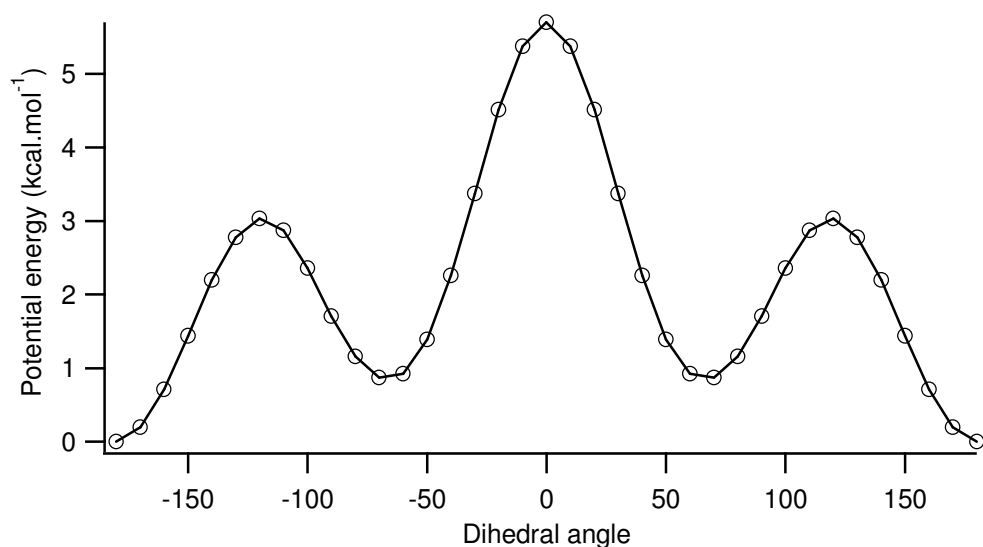


Figure S3: Potential of **•CH₂-CH₂-CH₂-CH₂-CH₃** internal rotor of 1-pentyl

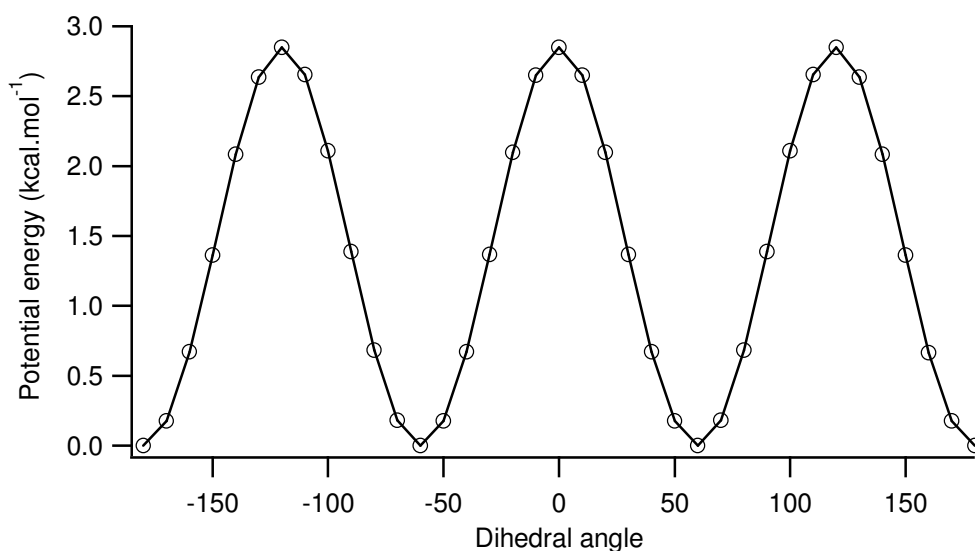


Figure S4: Potential of $\bullet\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ internal rotor of 1-pentyl

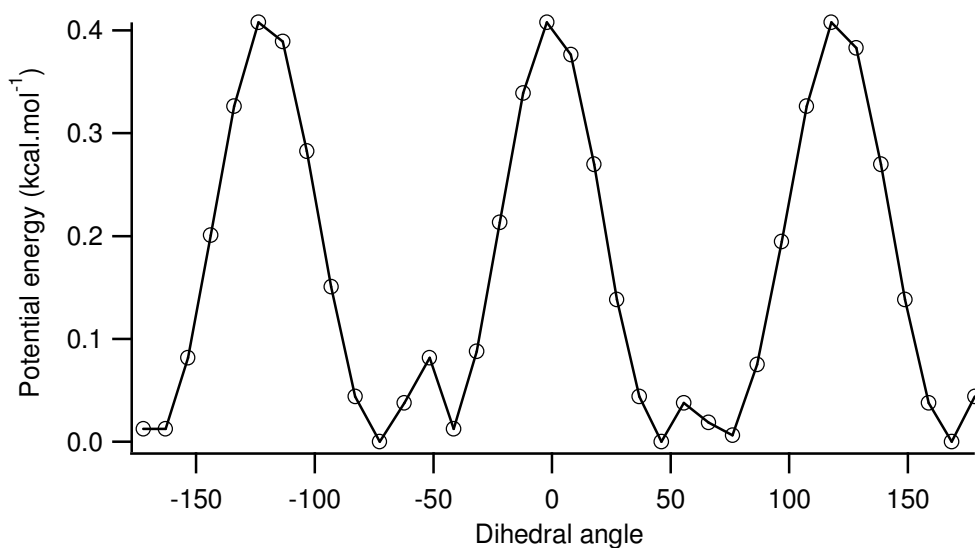


Figure S5: Potential of $\text{CH}_3\text{-CH}\bullet\text{-CH}_2\text{-CH}_2\text{-CH}_3$ internal rotor of 2-pentyl

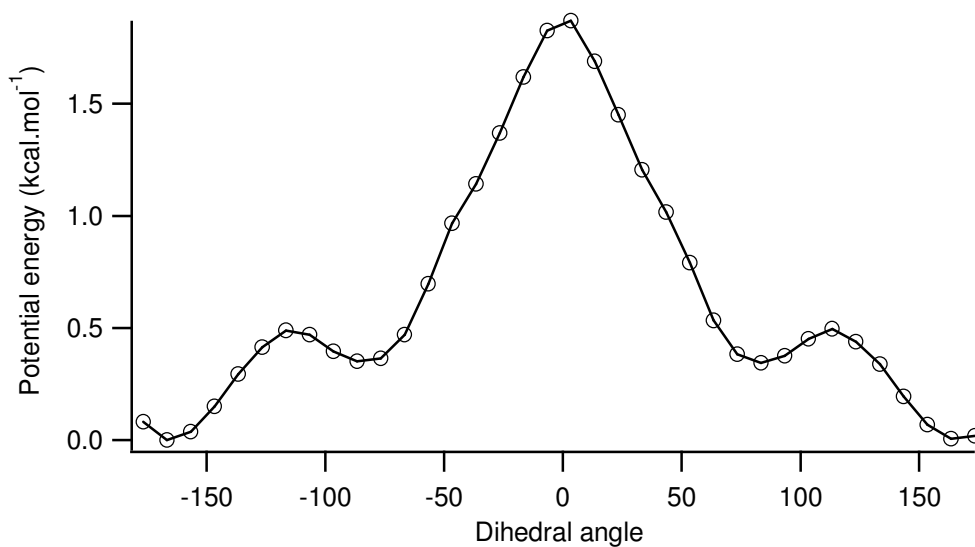


Figure S6: Potential of $\text{CH}_3\text{-CH}\bullet\text{-CH}_2\text{-CH}_2\text{-CH}_3$ internal rotor of 2-pentyl

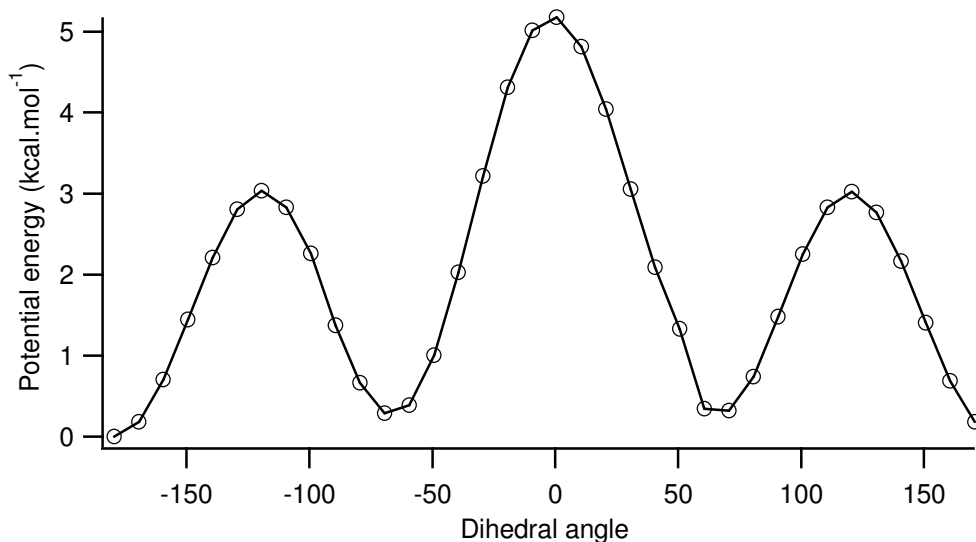


Figure S7: Potential of CH₃-CH•-CH₂-CH₂-CH₃ internal rotor of 2-pentyl

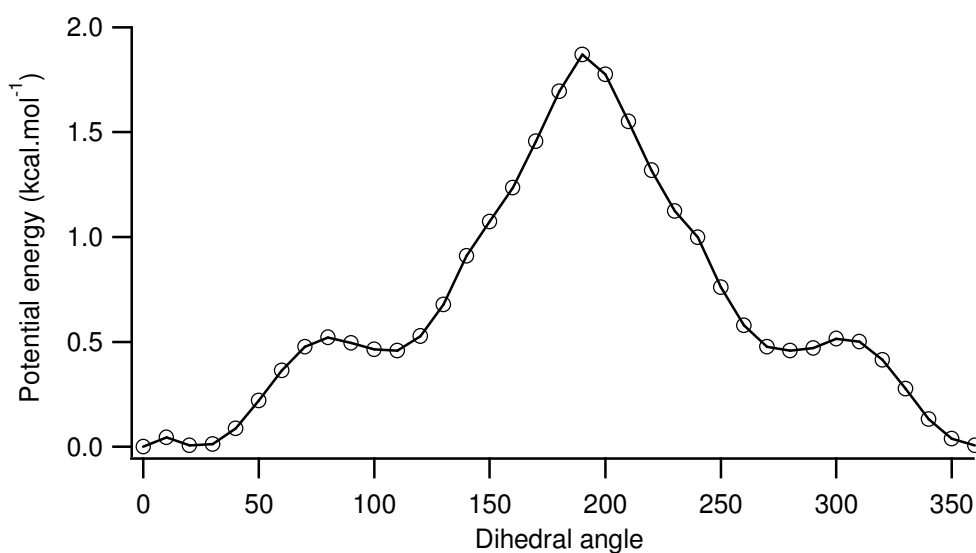


Figure S8: Potential of CH₃-CH₂-CH•-CH₂-CH₃ internal rotor of 3-pentyl

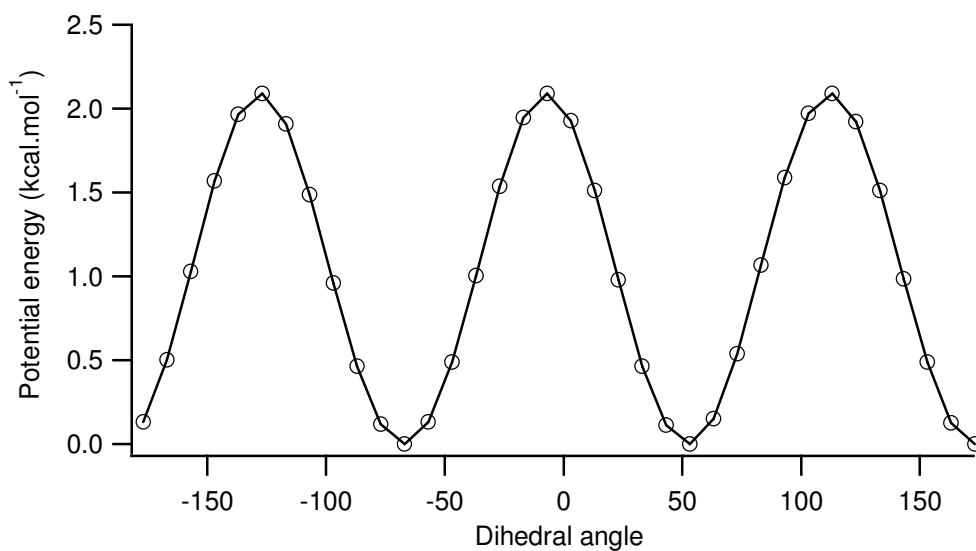


Figure S9: Potential of CH₃-cC₄H₈ internal rotor of TS 5ps of 1-pentyl

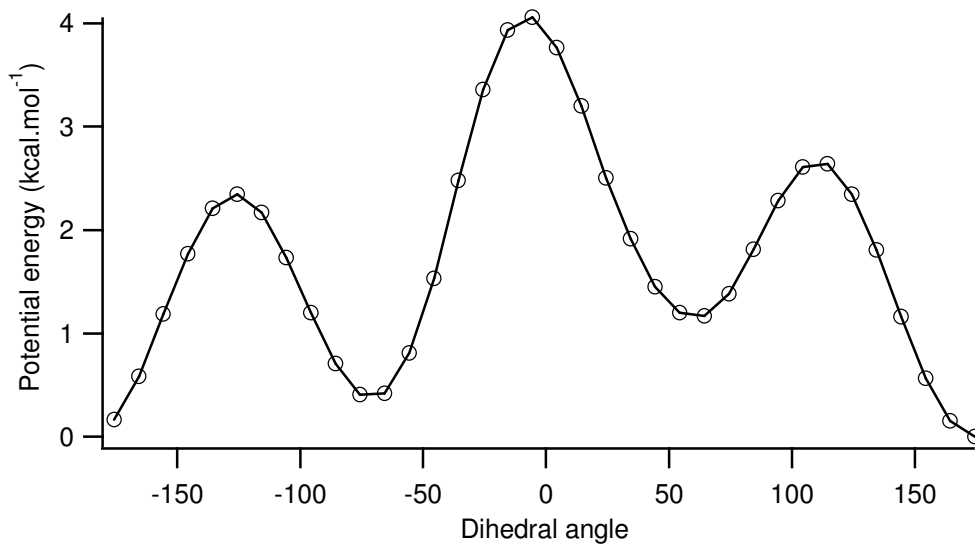


Figure S10: Potential of CH3-CH2-cC4H8 internal rotor of TS 5ps of 1-hexyl

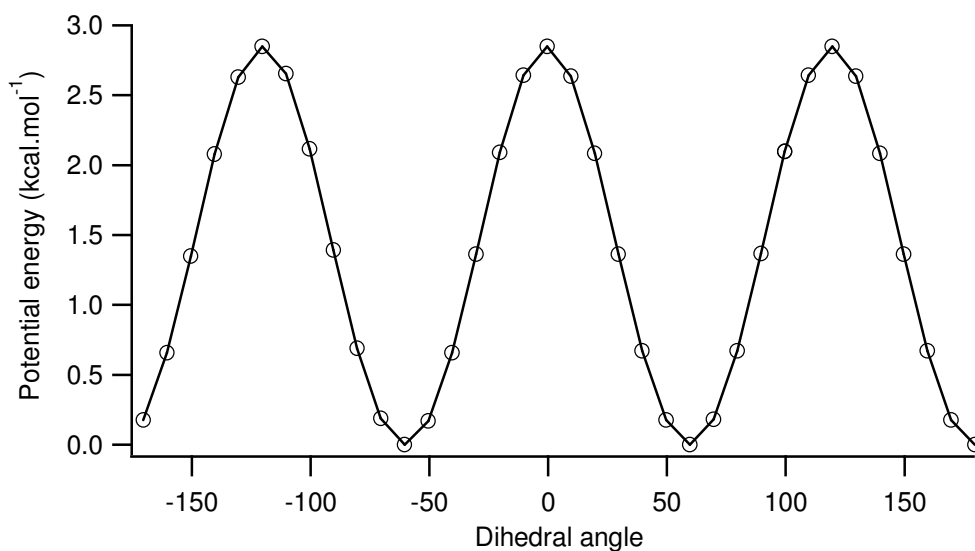


Figure S11: Potential of CH3-CH2-cC4H8 internal rotor of TS 5ps of 1-hexyl

Tableau 3: Forward and reverse reaction barrier heights (E_1 and E_{-1}) computed at the CBS-QB3 level of theory (kcal.mol^{-1} , 0 K), imaginary frequencies ν_i of the transition states (cm^{-1}) and calculated characteristic lengths (l , angstroms).

	<i>imaginary frequency (cm^{-1})</i>	E_1 (OK, kcal/mol)	E_{-1} (OK, kcal/mol)	l (angstroms)
1-pentyl \rightleftharpoons 2 pentyl (5sp)	1837.1	22.3	25.2	1.27
1-hexyl \rightleftharpoons 2 hexyl (6sp)	1679.4	15.3	18.3	1.17
1-hexyl \rightleftharpoons 3 hexyl (5sp)	1828.9	22.1	24.8	1.27
1-heptyl \rightleftharpoons 2-heptyl (7sp)	1621.0	14.7	17.6	1.19
1-heptyl \rightleftharpoons 3-heptyl (6sp)	1678.2	15.0	17.7	1.15
1-heptyl \rightleftharpoons 4-heptyl (5sp)	1833.4	22.0	24.7	1.26
2-heptyl \rightleftharpoons 3-heptyl (5ss)	1846.8	22.8	22.5	1.24
1-octyl \rightleftharpoons 2-octyl (8sp)	1609.8	18.8	21.7	1.34
1-octyl \rightleftharpoons 3-octyl (7sp)	1629.8	14.5	17.2	1.17
1-octyl \rightleftharpoons 4-octyl (6sp)	1680.3	15.0	17.7	1.15
1-octyl \rightleftharpoons 4-octyl (5sp)	1834.3	22.0	24.7	1.26
2-octyl \rightleftharpoons 3-octyl (6ss)	1697.5	15.7	15.4	1.12
2-octyl \rightleftharpoons 4-octyl (5ss)	1846.4	22.6	22.4	1.23

Table 4: Computed Small Curvature Tunneling transmission coefficients for n -heptyl H-atom shifts.

T	<i>SCT</i>		
	7ps	6ps	5ps
200	288	1870.1	930680
300	14.3	30.8	267.7
400	4.7	6.8	15.6
500	2.7	3.4	4.9
600	2	2.3	2.8
700	1.7	1.9	2.1
800	1.5	1.6	1.7
900	1.4	1.5	1.5
1000	1.3	1.4	1.4
1100	1.2	1.3	1.3
1200	1.2	1.2	1.3
1300	1.2	1.2	1.2
1400	1.1	1.2	1.2
1500	1.1	1.1	1.2
2000	1.1	1.1	1.1