

Supporting Information

Cartesian coordinates and energies (hartree) at 0 K including zero-point energy calculated using the CBS-QB3 method for reactants, products, pre-reactive complexes, and transition states.

1. Valeric acid (Trans)

Cartesian coordinates

C	1.905861071	2.4488175959	1.3331117064
H	2.1877420697	1.8670602677	2.2159626134
H	2.7421222801	3.1090777264	1.0885505381
H	1.0547002917	3.0779975558	1.6107110819
C	1.5548935136	1.532814983	0.1575483422
H	1.3109238331	2.1430213674	-0.7208166998
H	2.4355439609	0.9406149105	-0.1196989804
C	0.384890585	0.5918115313	0.4637213697
H	-0.499192979	1.1754308972	0.7397080559
H	0.6212341318	-0.0224924029	1.3386334193
C	0.0371515447	-0.3209743723	-0.7111559962
H	0.8951406271	-0.93622803	-1.0051959882
H	-0.2232027493	0.259860435	-1.6033305273
C	-1.1150094501	-1.2564390266	-0.4275647887
O	-1.7402555651	-1.3277333723	0.5991697714
O	-1.3851975288	-2.0447349287	-1.498796985
H	-2.1281102998	-2.6107805874	-1.2414696046

Energy: -346.442789

2. Valeric acid (Gauche)

Cartesian coordinates

C	2.2730714991	1.733578822	1.2249320451
H	2.2748729583	1.7326150639	2.3197192449
H	3.3142318888	1.7330291491	0.8915562979
H	1.8198454671	2.6732763865	0.8950392606
C	1.5098533027	0.5288305346	0.6684147218
H	1.5486911856	0.5461024407	-0.4246920676
H	2.0051613353	-0.3969157302	0.9874943111
C	0.0437151063	0.4955443095	1.1169919512
H	-0.4574080429	1.4106875301	0.7867203265
H	0.0006476736	0.4877517971	2.2118708463
C	-0.7368424266	-0.7125780325	0.5950080832
H	-1.7076256025	-0.7978006677	1.096881894
H	-0.2153140925	-1.6523296315	0.8037873552
C	-1.0281484361	-0.6579852895	-0.8884996259
O	-0.8633293191	0.288645762	-1.6153943076
O	-1.5405825747	-1.832264	-1.3335702822
H	-1.7217018932	-1.7118124987	-2.2777438025

Energy: -346.442997

3. OH

Cartesian coordinates

O	0.	0.	-0.1083565427
H	0.	0.	0.8668523415

Energy: -75.649720

4. H₂O

Cartesian coordinates

O	0.0576154277	0.0933934175	0.0451615063
H	-0.6993285699	0.0933934175	-0.5481644918
H	0.2384051482	-0.8405407577	0.186872441

Energy: -76.337482

5. P_{acid}

Cartesian coordinates

C	1.914483707	-0.5740623413	2.2848222938
H	2.6739824683	-1.3233888751	2.0406784788
H	2.3870059947	0.1847951492	2.9134829683
H	1.1420355108	-1.0665172881	2.8829974561
C	1.3202384748	0.0473572466	1.0183178411
H	0.5884827386	0.8124874884	1.2979961415
H	2.1096785899	0.5619083297	0.4571608745
C	0.6498624436	-0.9889903874	0.1080642435
H	-0.1467356869	-1.5008073644	0.657471986
H	1.378270862	-1.7580062908	-0.1694306298
C	0.0691656802	-0.3942532225	-1.1833279775
H	-0.24208981	-1.1921596668	-1.8681755417
H	0.8075324824	0.2057306453	-1.7247810775
C	-1.1434879508	0.4622833316	-0.9666991938
O	-1.912611146	0.3760714286	0.0216712588
O	-1.5323560139	1.3441723353	-1.7784792461

Energy: -345.770465

6. P_α

Cartesian coordinates

C	1.2521337783	2.7599291667	1.271846573
H	0.795230045	2.8756995382	2.2594646619
H	2.2586166607	3.1837184715	1.3184273778
H	0.6705356415	3.3582341436	0.5644922321
C	1.2925797827	1.2898260966	0.8485447994
H	1.7819233332	1.1968664889	-0.1261900283
H	1.8989429462	0.7153516348	1.5575763351
C	-0.1203139259	0.6654952149	0.7588903271
H	-0.725218648	1.2147374296	0.0335688697
H	-0.6027933929	0.7771586123	1.7413780284
C	-0.1039305242	-0.7702702035	0.387474399
H	0.3931637897	-1.4974246782	1.0202436242
C	-0.717904693	-1.2473280566	-0.8331268511
O	-1.2927472181	-0.5539617397	-1.6532614558
O	-0.5895383049	-2.5959326585	-0.9898850152
H	-1.0275026981	-2.811099763	-1.8255648174

Energy: -345.795090

7. P_β

Cartesian coordinates

C	-3.2237333814	0.1289266904	0.922847204
H	-3.5088747478	0.7059129999	0.0387920714
H	-4.0820765425	-0.4795459864	1.2181596016
H	-3.0196047724	0.8368984886	1.7308598018
C	-1.9965299885	-0.7417723782	0.6354133417
H	-1.7643659162	-1.3520532555	1.5244218669
H	-2.2465646613	-1.4810831352	-0.1440119946
C	-0.7920022497	0.0355781878	0.2271514075
H	-0.8240867195	1.1157032843	0.1554296743
C	0.4881713791	-0.651398519	-0.0915690779
H	0.3736438247	-1.3833797429	-0.9073705845
C	1.6078744687	0.2872545508	-0.4875251525
O	1.5450976775	1.4866834888	-0.559908199
O	2.7428808145	-0.4009968706	-0.7649477181
H	3.4104781321	0.2573794193	-1.0084078656
H	0.8549421041	-1.2568562067	0.7530684496

Energy: -345.786790

8. P_γ

Cartesian coordinates

C	-3.3592584014	0.4514919469	-0.5765608967
H	-3.422919253	1.1067816328	-1.4618589266
H	-4.2375214353	-0.1984569921	-0.5996244026
H	-3.4452724676	1.110432765	0.2957695859
C	-2.0903670726	-0.3292313637	-0.5503137971
H	-2.0772608214	-1.3186766594	-0.9983198457
C	-0.7893659148	0.3256275708	-0.2256705719
H	-0.9035262384	0.9865174888	0.642744778
C	0.3385940666	-0.6727372393	0.0399869362
H	0.4964949302	-1.328875131	-0.8230391455
C	1.6596741559	-0.0143592757	0.3597823535
O	1.8717087903	1.1699665915	0.4152366201
O	2.6267833196	-0.9374730506	0.5900605114
H	3.4360653313	-0.4429904935	0.7878108143
H	0.0872769403	-1.3384366595	0.8724648521
H	-0.4769348682	0.999005888	-1.0416689062

Energy: -345.787831

9. P_{methyl}

Cartesian coordinates

C	2.4870201373	-0.6788079908	-0.7417084107
H	2.727472614	-0.7937199736	-1.791381504
H	2.8966731598	-1.4090733908	-0.0514315863
C	1.8205803536	0.5525379005	-0.2317517966
H	2.5852303083	1.3047630458	0.0299296581
H	1.2187505565	1.0187559675	-1.0175619524
C	0.9482793174	0.3262324133	1.0180114654
H	0.6028075849	1.2928810002	1.3932867811
H	1.5626509232	-0.1224778553	1.8061066682
C	-0.2627751	-0.5776279292	0.7750037403
H	-0.7268280454	-0.8757886036	1.7217020329
H	0.0277466905	-1.5096344231	0.2800556982
C	-1.3487540665	0.0701843743	-0.0539029518
O	-1.382050931	1.2181461072	-0.4196368287
O	-2.3382417291	-0.8105224863	-0.343725161
H	-2.9982663617	-0.3218073426	-0.8577221575

Energy: -345.783244

10. Com1

Cartesian coordinates

C	2.4746007902	1.8023300657	1.735107301
H	2.4747997134	1.8024030729	2.8298575677
H	3.5160472447	1.8023733024	1.4031000791
H	2.0208535933	2.7411695304	1.4034741759
C	1.7136277905	0.5962735558	1.1783275539
H	1.7510278806	0.6147740399	0.0851522008
H	2.2115527171	-0.3286749887	1.4949832043
C	0.2487723111	0.5586863094	1.6309570968
H	-0.2544733834	1.4769072708	1.3127141414
H	0.2090883126	0.5402918188	2.7257330086
C	-0.5324158216	-0.6470880193	1.1040071764
H	-1.5054822187	-0.7315246978	1.6016959712
H	-0.012451685	-1.5880919703	1.3099083098
C	-0.8259758024	-0.6070144018	-0.3800574306
O	-0.667475692	0.3855943323	-1.0783220444
O	-1.3005911572	-1.7455246607	-0.857542748
H	-1.4520570424	-1.5715542082	-1.8264947092
O	-1.2410648383	-0.5463542723	-3.1697190959
H	-1.7575072392	0.2730785766	-3.1055030275

Energy: -422.099038

11. Com2

Cartesian coordinates

C	0.1674622856	2.7682849179	1.0986776104
H	-0.6093666428	3.0824534298	1.803170558
H	1.0769689805	3.3260711024	1.3372081768
H	-0.1497299634	3.0535140622	0.0925829546
C	0.4080481824	1.2583861219	1.1744918149
H	1.188152572	0.984160716	0.4565842152
H	0.7905595076	0.9892100721	2.1671724897
C	-0.859320403	0.4450473076	0.883295552
H	-1.2609753401	0.7452252433	-0.0880244402
H	-1.6243135401	0.6894883333	1.6279109205
C	-0.6428682803	-1.0699821179	0.8996624163
H	-1.6023624259	-1.6008237689	0.8749503328
H	-0.1476928258	-1.4010068783	1.8176574842
C	0.1498010685	-1.5989536861	-0.2716438519
O	0.3917064182	-1.0150535487	-1.3058537355
O	0.5639379578	-2.8643042589	-0.0678012818
H	1.0317310861	-3.1410569588	-0.870653928
O	-0.2125713832	1.5992751472	-2.3607541198
H	0.0237075307	0.6967306705	-2.0501869171

Energy: -422.100912

12. Com3

Cartesian coordinates

C	2.3361998006	2.3051059637	1.2109732868
H	2.3359726418	2.3068207854	2.3056165751
H	3.3778716758	2.3023475392	0.8796437572
H	1.8842868752	3.2441237174	0.8774205912
C	1.5738367741	1.0986187348	0.6570336359
H	1.6142058066	1.1152302932	-0.4366844824
H	2.0697764771	0.1738165247	0.9762626442
C	0.1084968455	1.0644306781	1.1072205154
H	-0.3959405301	1.9793233808	0.7812176369
H	0.0666205178	1.0519885965	2.2016770223
C	-0.6685788344	-0.1466686298	0.5858116431
H	-1.6438706223	-0.2248332795	1.0820989255
H	-0.1562548144	-1.0893252194	0.8001924028
C	-0.9595662652	-0.0867482015	-0.8940051113
O	-0.8747663956	0.8690674925	-1.6156652243
O	-1.3874621419	-1.3008465306	-1.371894908
H	-1.5837861987	-1.1775671312	-2.3131673129
O	-0.3741807436	-3.5842260494	0.1507289541
H	-0.8199375027	-2.9623157799	-0.4618321537

Energy: -422.097203

13. TS_{acid}

Cartesian coordinates

C	2.4479683345	1.8149527952	1.7188627983
H	2.4483815652	1.8144843906	2.8135558063
H	3.4892618323	1.8150131246	1.3865998927
H	1.9941473364	2.7538726139	1.3876023767
C	1.6872358877	0.6088724956	1.1618058998
H	1.7261452827	0.6275311683	0.0683480136
H	2.1848665714	-0.3161916988	1.4780578438
C	0.2221147184	0.5715210128	1.6135174751
H	-0.2818789916	1.4896172137	1.2962238437
H	0.181905492	0.5533794605	2.7083740591
C	-0.5583386608	-0.6379749808	1.0912859303
H	-1.5470185292	-0.6938576428	1.5612887127
H	-0.0554813285	-1.5797909973	1.3291458
C	-0.8217087704	-0.6542784328	-0.4042819502
O	-0.7258664977	0.4129408523	-1.0639932875
O	-1.1657408012	-1.7540862315	-0.9444865326
H	-1.2857878809	-1.3698862137	-2.0670288102
O	-1.2015706305	-0.5742629931	-2.9995463132
H	-1.972746971	0.0105382198	-2.9850993921

Energy: -422.088625

14. TS_{a1}

Cartesian coordinates

C	2.7532832267	2.0775681201	0.0362919608
H	2.7469065874	2.1012640059	1.1302264785
H	3.7961962589	2.0387835551	-0.2881907654
H	2.3295350581	3.022110408	-0.3190108868
C	1.9656609731	0.8773235328	-0.4942134056
H	2.0114383749	0.8618506302	-1.589552047
H	2.4236495036	-0.0541986259	-0.1480103517
C	0.4994928937	0.8874728606	-0.0469829046
H	0.0129212893	1.8126499905	-0.3862955319
H	0.4445865127	0.8854141268	1.046146373
C	-0.2907050014	-0.3044881243	-0.5785270373
H	-0.3142605676	-0.3618762494	-1.6680420187
C	-1.6568229109	-0.4440094521	0.0296132217
O	-1.8647641326	-0.7699071675	1.1752535312
O	-2.6493094772	-0.1529019063	-0.8370188387
H	-3.4838077087	-0.2630673313	-0.3550874313
H	0.2901831887	-1.292131688	-0.2129228236
O	0.7652354341	-2.2324191602	0.6340530242
H	0.1079018207	-2.0721745725	1.3353462611

Energy: -422.091900

15. TS_{a2}

Cartesian coordinates

C	2.166670208	2.2162927009	1.0809326014
H	2.1667207569	2.2162258266	2.175546846
H	3.2084123141	2.2163264209	0.7500844387
H	1.7132045547	3.155327072	0.7486061028
C	1.4101901432	1.0079076611	0.5241527782
H	1.4539484378	1.0216809509	-0.5687492086
H	1.8947392964	0.080798723	0.8475427662
C	-0.0598699935	0.980047629	0.9658773868
H	-0.5686561442	1.8802961465	0.5983950871
H	-0.1160803071	1.0088312112	2.0588685999
C	-0.8333480262	-0.2347334659	0.4797092739
H	-1.7964371076	-0.3680244391	0.9822195317
C	-1.047286672	-0.3192160485	-1.0065679015
O	-0.910987054	0.5782189678	-1.7967700181
O	-1.4474745663	-1.5645160453	-1.3845161341
H	-1.5897285445	-1.5319111125	-2.342578576
H	-0.2407769044	-1.2139709847	0.7953496276
O	0.3758059134	-2.4540960837	0.8783195011
H	-0.0822346545	-2.8442253845	0.1138231596

Energy: -422.092132

16. TS_β**Cartesian coordinates**

C	2.3732165792	1.3351711896	1.2735013948
H	2.373202526	1.3351564705	2.3679411782
H	3.4137510231	1.3351202375	0.9395899554
H	1.9007887658	2.2602817362	0.9363101041
C	1.6141050701	0.1270276416	0.7181002015
H	1.6766269337	0.1266244127	-0.3744225418
H	2.0906104779	-0.803968202	1.0581880012
C	0.1517237029	0.1070612199	1.1390021075
H	0.0434740716	0.1505171676	2.227426953
C	-0.7006667688	-1.0173694678	0.5710990032
H	-1.7089384443	-0.987363367	0.999872393
H	-0.2913665642	-1.9978970157	0.8396177073
C	-0.8826438088	-0.9879537118	-0.9317295578
O	-0.7152419838	-0.037734963	-1.6602208725
O	-1.3025462914	-2.1812972049	-1.4001645764
H	-1.438696516	-2.0763405749	-2.3542506355
H	-0.3325694054	1.1515388959	0.8028251313
O	-0.7702926177	2.255688268	0.1441121976
H	-0.756644373	1.8294602094	-0.7327511312

Energy: -422.096645**17. TS_γ****Cartesian coordinates**

C	-0.3037889113	-1.2395803544	-1.1322446811
C	-0.2422592311	-1.3118724785	0.3892082562
H	0.8006027144	-1.3535005356	0.7174433217
H	-0.7036414413	-2.2574853498	0.7013539899
C	-0.9550317064	-0.1699924291	1.1204403499
H	-1.9207231855	0.0658216098	0.6633099766
H	-1.1812857135	-0.456669588	2.1539247857
C	-0.1535604709	1.1082336353	1.2152122242
O	1.0201630166	1.2373257084	0.9555723864
O	-0.9024938427	2.12917551	1.6783322951
H	-0.3210046324	2.902926674	1.7307980804
H	-1.3338685082	-1.0970562411	-1.479261333
C	0.3755478575	-2.3958838808	-1.8470287283
H	-0.1127758463	-3.347952766	-1.6057855579
H	0.3392259211	-2.2648138889	-2.9303553064
H	1.4261506345	-2.4748456263	-1.5549332373
H	0.234246861	-0.2598971301	-1.5186940065
O	1.0135062447	0.8324724594	-1.9223306591
H	1.3982246207	1.0062564636	-1.0439174185

Energy: -422.095574

18. TS_{methyl1}**Cartesian coordinates**

C	2.0388861074	-0.2977718273	1.6915520034
H	2.0391816705	-0.2976051167	2.7827362231
H	3.0578477995	-0.2977742554	1.2975434137
C	1.1302980947	0.7434774095	1.0681919725
H	0.1237034965	0.6160514265	1.4779646918
H	1.4550462194	1.7495420785	1.3670330651
C	1.0864954009	0.646913829	-0.4691935172
H	1.1903963724	-0.4012135544	-0.7593285379
H	1.9412126064	1.1781217745	-0.8983820318
C	-0.2021614329	1.1978315475	-1.0799409573
H	-0.1195224238	1.2931398109	-2.1680197425
H	-0.4365327922	2.2033913784	-0.7138173951
C	-1.4013174549	0.3164643541	-0.8098207214
O	-1.3920323089	-0.7505854652	-0.2400181507
O	-2.538535497	0.8535603985	-1.2985230407
H	-3.2521834276	0.2284449921	-1.0996935799
H	1.6132430996	-1.3972746237	1.3812381076
O	0.9720070826	-2.4213359277	0.8314225532
H	0.142888875	-1.9694278332	0.5849422112

Energy: -422.093550**19. TS_{methyl2}****Cartesian coordinates**

C	-0.5642387428	-1.8648761026	1.7341444618
H	-1.3842556048	-2.024629912	2.4375003574
H	-0.4662501676	-2.7246031461	1.0667323185
C	-0.6231630742	-0.5371701011	1.0026291584
H	-1.529027305	-0.5142216533	0.3845952975
H	-0.7155447456	0.2761106502	1.7319230633
C	0.6044249209	-0.2934721323	0.1157565026
H	0.6619202309	-1.078379581	-0.6454824744
H	1.4988619737	-0.3786898182	0.7394206041
C	0.6105183798	1.0699395862	-0.5755965826
H	1.5847666905	1.2700314381	-1.0354338437
H	0.4538718419	1.8848807388	0.1390931913
C	-0.4214385837	1.2063351876	-1.6726377346
O	-1.1359581255	0.3319053685	-2.0943833663
O	-0.4496530213	2.4671429712	-2.1693274976
H	-1.1164039664	2.4711624098	-2.8723111083
H	0.4034464871	-1.8639374579	2.4189009565
O	1.6963240694	-1.8338239299	2.9645146669
H	2.0862937848	-2.5240575736	2.4028563794

Energy: -422.089960

