Ab initio modelling of the anomeric and *exo*-anomeric effects in 2-methoxytetrahydropyran and 2-methoxythiane; corrected for intramolecular BSSE

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Torsional PES scans of MTHP and MT

We present torsional PES scans of 2-methoxytetrahydropyran (MTHP) and 2-methoxythiane (MT) around the glycosidic linkage C1-O1 calculated with different methods. The scans are depicted in Figures 1 to 4. Clearly, DFT with the B3LYP[1] functional and with the selected basis sets does not capture the ETG minima in MTHP and MT and the location of ATG is problematic as well. Moreover, the minimum for AGG in MTHP is too shallow and hard to localize. However, even MP2 in cc-pVDZ basis indicates a false shallow minimum in MTHP around $\phi \approx 310°$, but the position of the AGG minimum is consistent with MP2 results in larger basis sets. The M062X functional[2] yields results more consistent with MP2. The PBE functional[3] performs better than B3LYP, yet the ATG minimum is shallower than the MP2 and M062X ones and the EGT minima are not localized. The data used in Figures 1 to 4 is collected below.

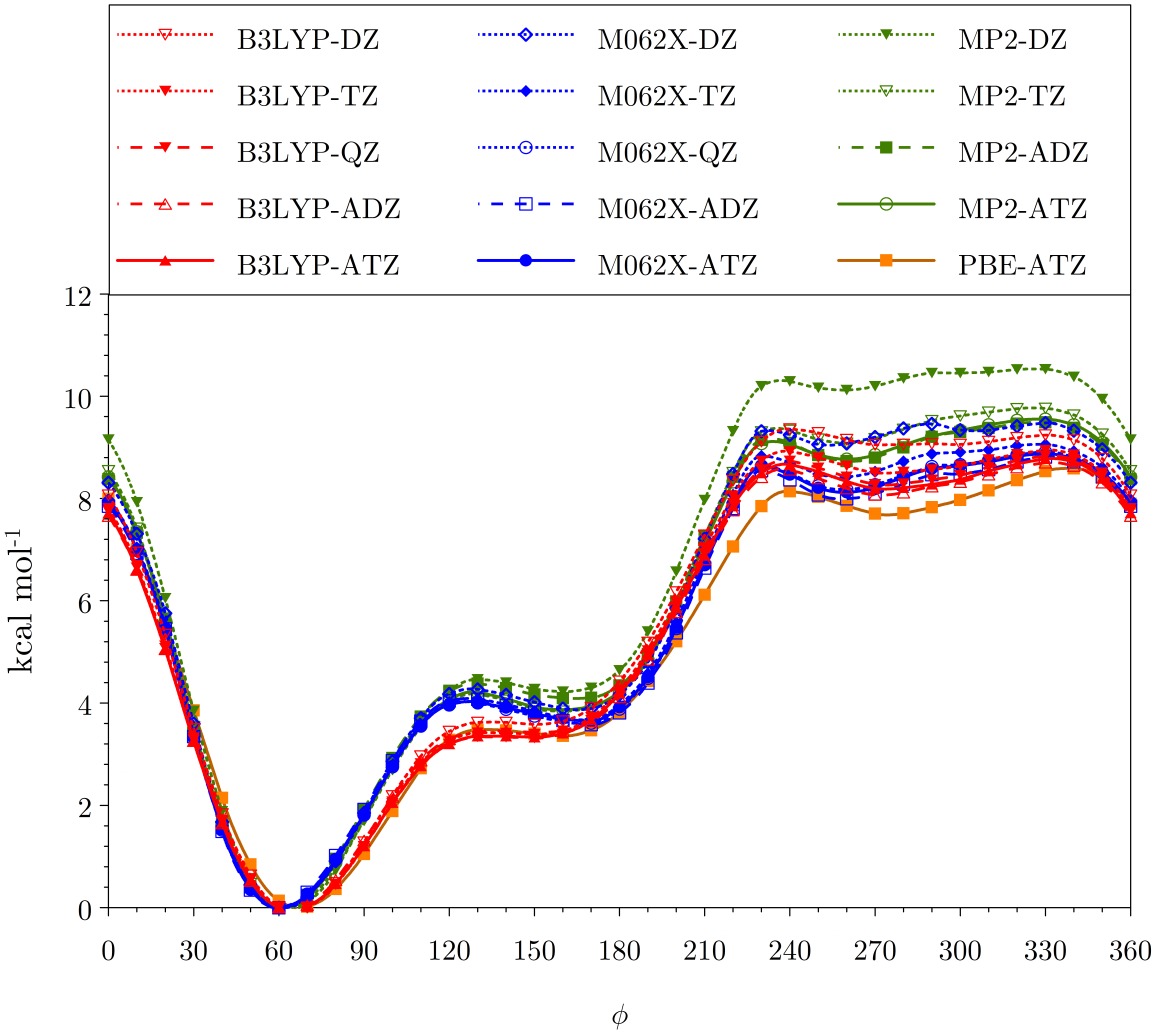


Figure S 1: Torsional PES scans around the glycosidic linkage C1-O1 of 2-methoxytetrahydropyran in axial form for different methods.

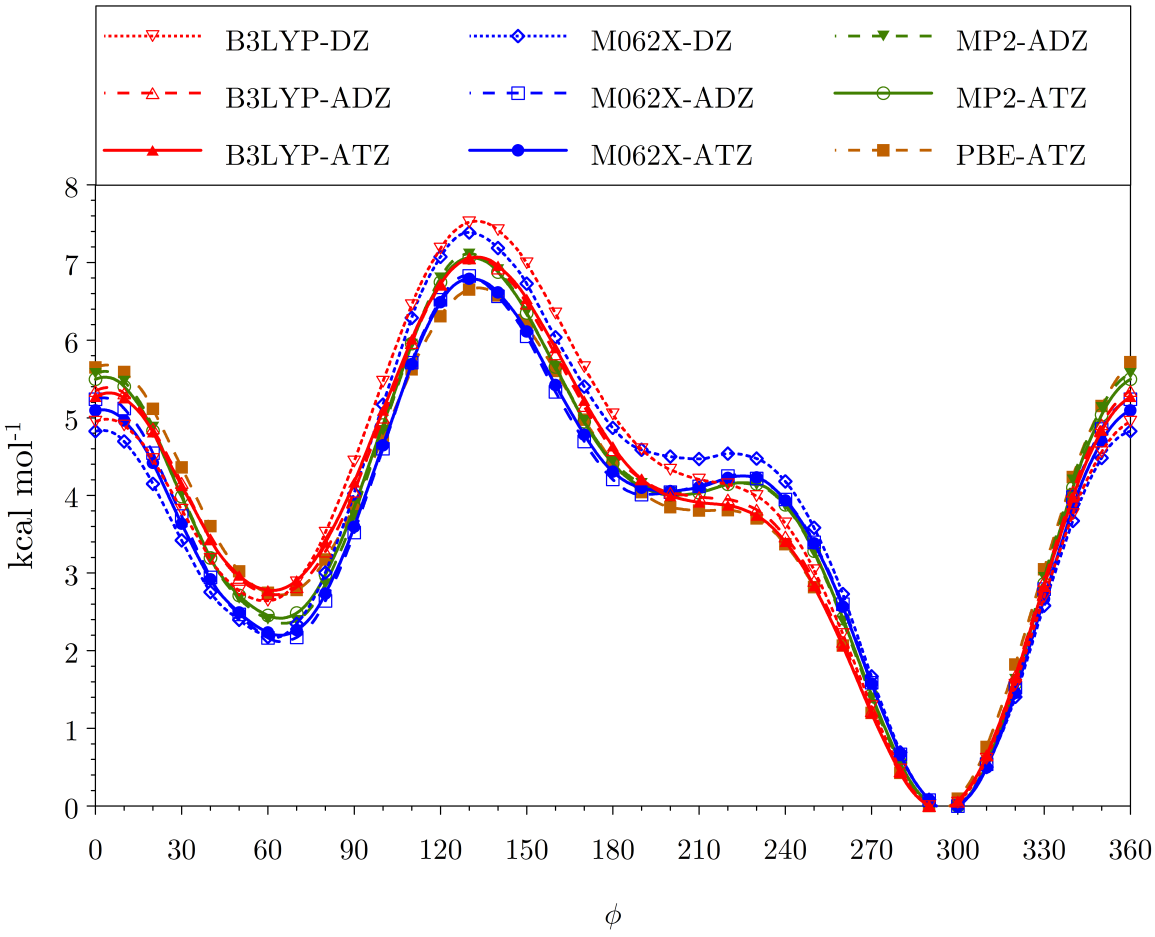


Figure S 2: Torsional PES scans around the glycosidic linkage C1-O1 of 2-methoxytetrahydropyran in equatorial form for different methods.

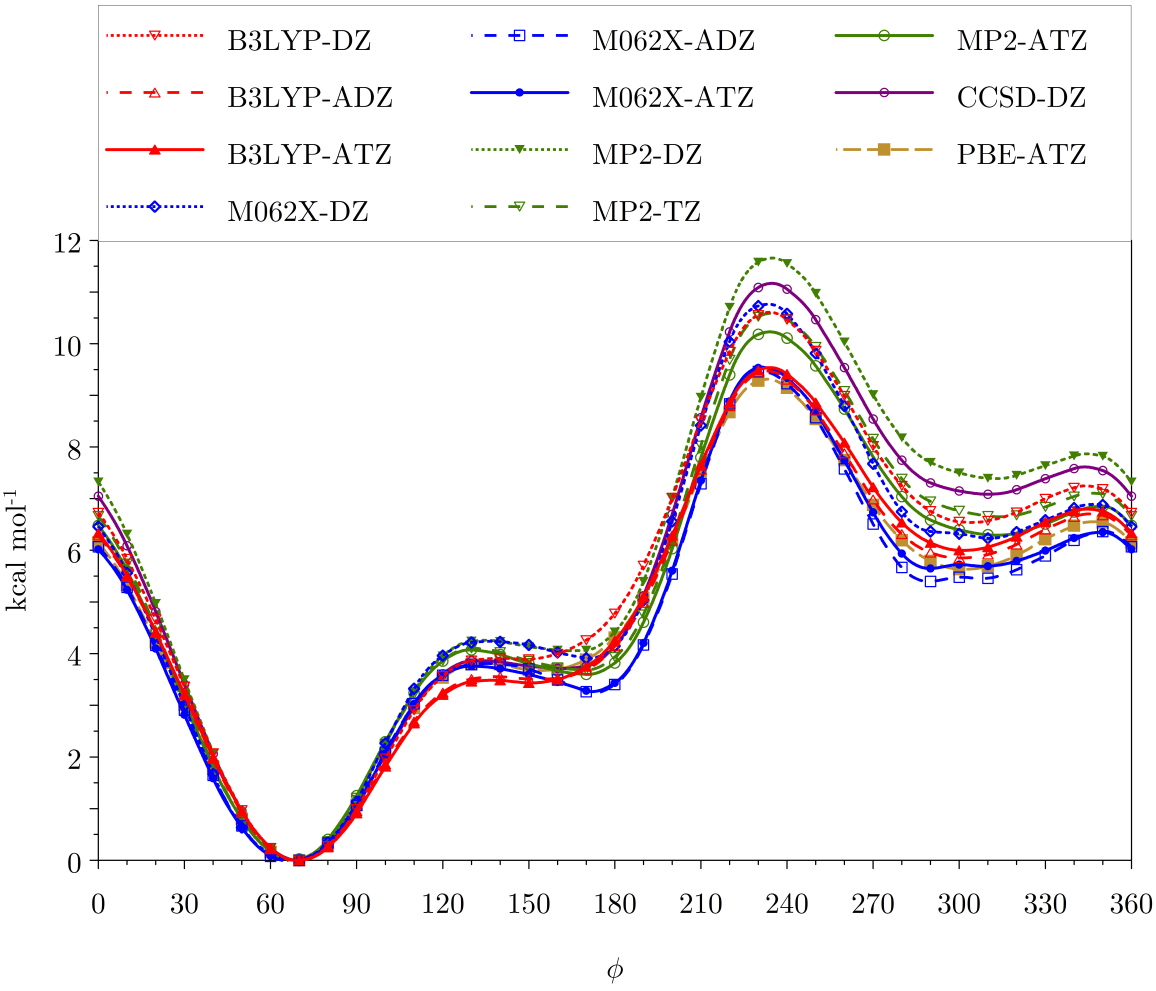


Figure S 3: Torsional PES scans around the glycosidic linkage C1-O1 of 2-methoxythiane in axial form for different methods.

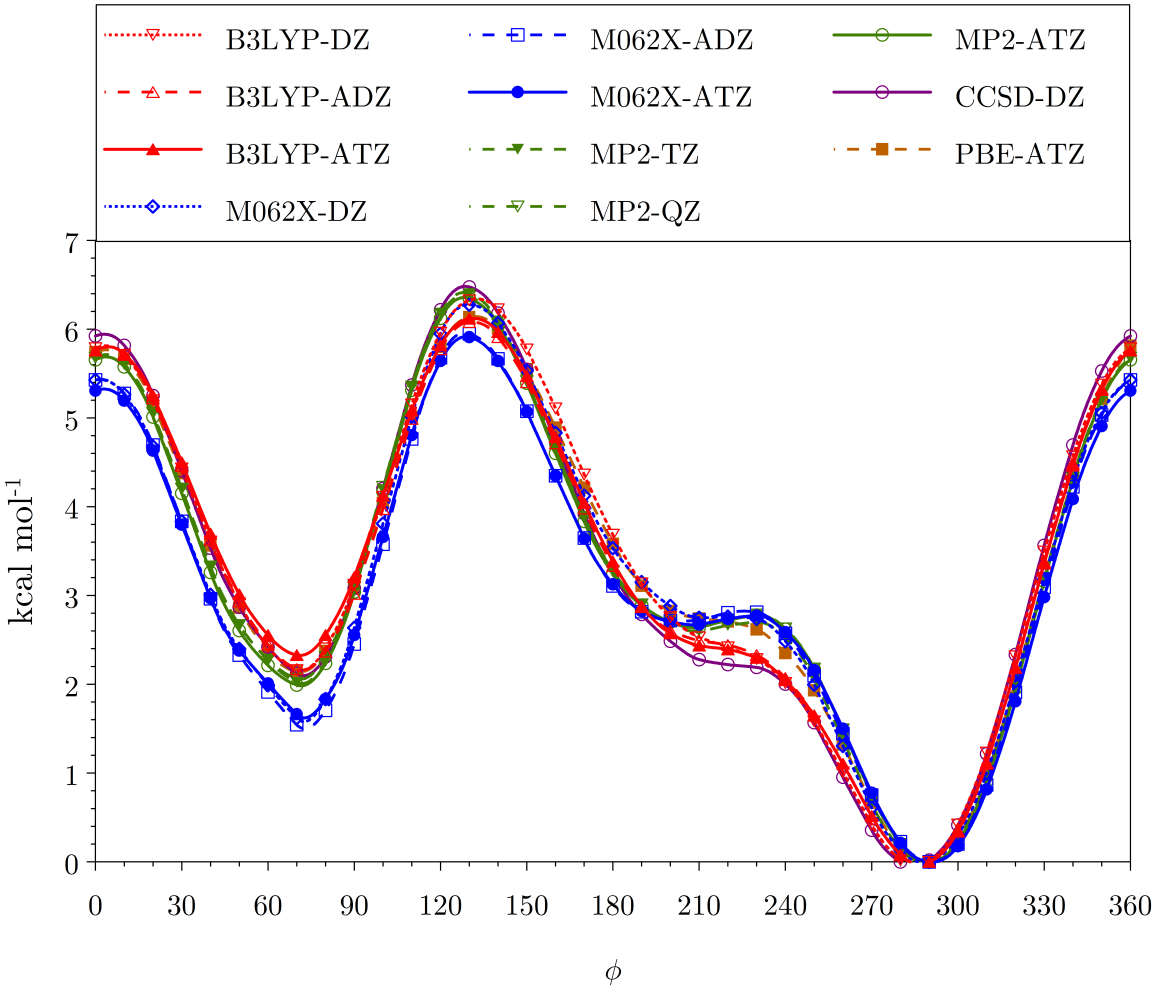
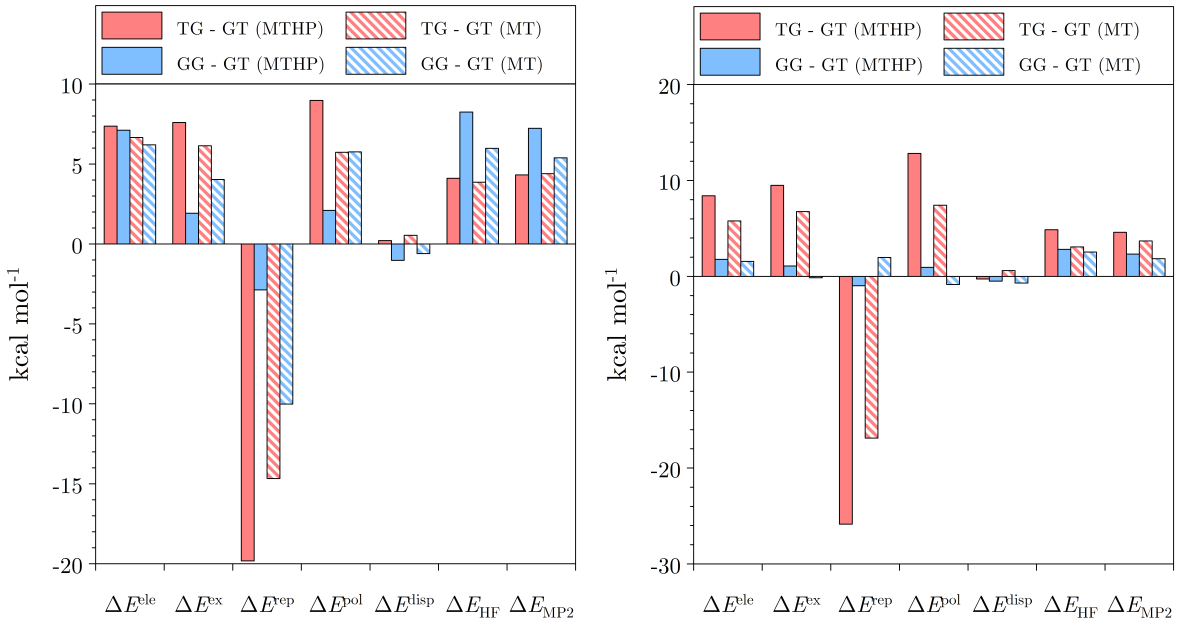


Figure S 4: Torsional PES scans around the glycosidic linkage C1-O1 of 2-methoxythiane in equatorial form for different methods.



(a) axial **(b)** equatorial

Figure S 5: Differences of ROMP2/aug-cc-pVTZ EDA contributions and ROMP2/aug-cc-pVTZ and ROHF/aug-cc-pVTZ interaction energies of the TG,GG conformers with respect to the most stable GT conformer.

Table S 1: Calculated relative energies of the rotation about the C1-O1 linkage in axial 2-methoxytetrahydropyran. All energies are in kcal mol^{-1}.

ϕ	B3LYP-DZ	B3LYP-TZ	B3LYP-QZ	B3LYP-ADZ	B3LYP-ATZ	M062X-DZ	M062X-TZ	M062X-QZ	M062X-ADZ	M062X-ATZ	MP2-DZ	MP2-TZ	MP2-ADZ	MP2-ATZ	PBE-ATZ
0.00	8.063213	7.806137	7.755937	7.655537	7.712012	8.308140	7.981838	7.912813	7.850063	7.912813	9.148994	8.540316	8.377165	8.421090	7.991105
10.00	6.946258	6.695457	6.645257	6.601332	6.607607	7.310410	7.040584	6.984108	6.927633	6.996658	7.925363	7.417085	7.329235	7.348060	7.002840
20.00	5.339850	5.120424	5.070224	5.051399	5.038849	5.754203	5.509476	5.421626	5.453001	5.434176	6.049129	5.647527	5.641252	5.616152	5.577927
30.00	3.494992	3.325766	3.281841	3.256741	3.250466	3.595592	3.419891	3.332041	3.344591	3.344591	3.846593	3.539117	3.507742	3.501467	3.857421
40.00	1.832109	1.713083	1.681708	1.644058	1.662883	1.675433	1.587583	1.518557	1.493457	1.531107	1.882509	1.687983	1.625233	1.644058	2.147459
50.00	0.633578	0.571028	0.545928	0.520827	0.533378	0.445527	0.401602	0.363952	0.345127	0.370227	0.558478	0.470627	0.407877	0.432977	0.845888
60.00	0.012550	0.006275	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.135745
70.00	0.000000	0.000000	0.018825	0.050200	0.018825	0.207076	0.225901	0.263551	0.301201	0.263551	0.094125	0.150601	0.251001	0.213351	0.000000
80.00	0.483177	0.445527	0.458077	0.539653	0.464352	0.909879	0.884779	0.941255	1.016555	0.934979	0.727903	0.784379	0.953805	0.878504	0.364461
90.00	1.280106	1.198531	1.192256	1.311481	1.204806	1.851134	1.794659	1.813484	1.920159	1.826034	1.719358	1.713083	1.926434	1.813484	1.046893
100.00	2.183710	2.070760	2.039385	2.164885	2.051935	2.861414	2.773563	2.754738	2.873964	2.767288	2.786113	2.704538	2.924164	2.779838	1.887482
110.00	2.961814	2.817488	2.761013	2.873964	2.767288	3.702268	3.589317	3.551667	3.645792	3.557942	3.683443	3.532842	3.733643	3.583042	2.723532
120.00	3.444991	3.263016	3.193990	3.294391	3.200265	4.179170	4.016019	3.965819	4.041119	3.965819	4.254470	4.034844	4.229370	4.072494	3.281915
130.00	3.620692	3.419891	3.338316	3.444991	3.350866	4.267020	4.078769	4.003469	4.072494	4.016019	4.461546	4.172895	4.379971	4.210545	3.478181
140.00	3.620692	3.413616	3.332041	3.451266	3.350866	4.160345	3.972094	3.877969	3.953269	3.909344	4.398796	4.053669	4.292121	4.085045	3.464990
150.00	3.583042	3.388516	3.313216	3.426166	3.332041	4.016019	3.840318	3.746193	3.821493	3.790118	4.273295	3.890519	4.166620	3.921894	3.402240
160.00	3.645792	3.457542	3.394791	3.451266	3.407341	3.890519	3.714818	3.633242	3.658342	3.695993	4.223095	3.840318	4.097595	3.871694	3.359561
170.00	3.903069	3.721093	3.664618	3.639517	3.670893	3.890519	3.670893	3.608142	3.576767	3.645792	4.298396	3.915619	4.103870	3.934444	3.466900
180.00	4.423896	4.254470	4.191720	4.110145	4.191720	4.166620	3.959544	3.884244	3.808943	3.915619	4.637247	4.216820	4.342321	4.216820	3.819507
190.00	5.183175	5.026299	4.950999	4.844323	4.938449	4.800398	4.574497	4.486646	4.392521	4.505472	5.396526	4.888248	4.957274	4.844323	4.426509
200.00	6.168354	5.980104	5.885978	5.773028	5.860878	5.854603	5.572227	5.459276	5.371426	5.471826	6.569956	5.948728	5.986379	5.867153	5.206059
210.00	7.279035	7.040584	6.927633	6.808408	6.883708	7.210009	6.846058	6.708007	6.638982	6.714282	7.969288	7.260210	7.241385	7.128434	6.116786
220.00	8.345790	8.050863	7.906538	7.762212	7.850063	8.477566	8.069689	7.893988	7.806137	7.900263	9.312145	8.502666	8.421090	8.326965	7.060245
230.00	9.111344	8.734842	8.565416	8.414815	8.496391	9.312145	8.828967	8.634441	8.546591	8.621891	10.19692	9.299594	9.142719	9.073693	7.849483
240.00	9.356070	8.916818	8.734842	8.559141	8.659541	9.243119	8.697192	8.490116	8.364615	8.465015	10.29104	9.330970	9.086243	9.054868	8.139389
250.00	9.280569	8.797592	8.596791	8.389715	8.521491	9.054868	8.477566	8.245389	8.069689	8.207739	10.16554	9.155269	8.847792	8.854067	8.031503
260.00	9.148794	8.634441	8.421090	8.195189	8.333240	9.073693	8.421090	8.176364	7.994388	8.119889	10.12162	9.079968	8.728567	8.766217	7.855239
270.00	9.048393	8.502666	8.276765	8.069689	8.195189	9.199194	8.521491	8.264215	8.088514	8.214014	10.19692	9.167819	8.797592	8.854067	7.703998
280.00	9.054668	8.515216	8.289315	8.113614	8.207739	9.368620	8.722292	8.446190	8.283040	8.414815	10.34752	9.349795	8.998393	9.042318	7.709847
290.00	9.067218	8.565416	8.364615	8.232839	8.276765	9.456470	8.872892	8.621891	8.465015	8.584241	10.45420	9.519221	9.205469	9.218019	7.828782
300.00	9.054668	8.634441	8.452465	8.320690	8.370890	9.337245	8.904268	8.659541	8.477566	8.640716	10.45420	9.613346	9.299594	9.330970	7.972248
310.00	9.111143	8.759942	8.609341	8.465015	8.534041	9.330970	8.948193	8.741117	8.565416	8.716017	10.47302	9.688646	9.374895	9.437645	8.158298
320.00	9.186444	8.866617	8.741117	8.603066	8.672091	9.412545	9.029768	8.847792	8.716017	8.822692	10.52322	9.757672	9.462745	9.525496	8.358151
330.00	9.236644	8.941918	8.828967	8.697192	8.772492	9.475295	9.054868	8.910543	8.810142	8.872892	10.52950	9.763947	9.487845	9.550596	8.534217
340.00	9.142519	8.854067	8.766217	8.634441	8.716017	9.324695	8.923093	8.803867	8.716017	8.778767	10.37890	9.632171	9.381170	9.437645	8.586640
350.00	8.778567	8.502666	8.433640	8.308140	8.389715	8.960743	8.609341	8.508941	8.421090	8.496391	9.945923	9.255669	9.048593	9.092518	8.403690
360.00	8.063213	7.806137	7.755937	7.655537	7.712012	8.308140	7.981838	7.912813	7.850063	7.912813	9.148994	8.540316	8.377165	8.421090	7.897293

Table S 2: Calculated relative energies of the rotation about the C1-O1 linkage in equatorial 2-methoxytetrahydropyran. All energies are in kcal mol^{-1}.

ϕ	B3LYP-DZ	B3LYP-ADZ	B3LYP-ATZ	M062X-DZ	M062X-ADZ	M062X-ATZ	MP2-ADZ	MP2-ATZ	PBE-ATZ
360.00	4.950999	5.346326	5.271025	4.825498	5.239650	5.095324	5.572227	5.496926	5.717212
350.00	4.555672	4.913348	4.831773	4.480371	4.856873	4.693722	5.132975	5.038849	5.151138
340.00	3.758743	4.047394	3.972094	3.670893	3.978369	3.840318	4.197995	4.097595	4.234155
330.00	2.691988	2.892789	2.836314	2.579037	2.792388	2.666888	2.942989	2.861414	3.047890
320.00	1.562482	1.675433	1.650333	1.405607	1.524832	1.455807	1.631508	1.575033	1.821109
310.00	0.608678	0.652603	0.652603	0.502002	0.539653	0.495727	0.564753	0.539653	0.761340
300.00	0.043925	0.056475	0.069025	0.000000	0.000000	0.000000	0.000000	0.000000	0.094125
290.00	0.000000	0.000000	0.000000	0.081575	0.075300	0.081575	0.018825	0.031375	0.000000
280.00	0.470627	0.445527	0.426702	0.690253	0.665153	0.665153	0.533378	0.558478	0.426702
270.00	1.286381	1.223631	1.192256	1.669158	1.587583	1.575033	1.393057	1.430707	1.198531
260.00	2.215086	2.114685	2.058210	2.729638	2.597862	2.566487	2.384511	2.415887	2.064485
250.00	3.037115	2.899064	2.830039	3.583042	3.394791	3.382241	3.263016	3.281841	2.817488
240.00	3.639517	3.470092	3.401066	4.179170	3.946994	3.934444	3.865418	3.877969	3.369691
230.00	3.990919	3.815218	3.739918	4.474096	4.216820	4.229370	4.135245	4.147795	3.702268
220.00	4.141520	3.946994	3.871694	4.536847	4.248195	4.223095	4.141520	4.141520	3.808943
210.00	4.204270	3.978369	3.909344	4.467821	4.116420	4.103870	4.053669	4.034844	3.802668
200.00	4.329771	4.034844	3.990919	4.499197	4.041119	4.053669	4.041119	4.003469	3.846593
190.00	4.593322	4.204270	4.210545	4.587047	4.009744	4.097595	4.154070	4.110145	4.041119
180.00	5.045124	4.580772	4.630972	4.869423	4.204270	4.304671	4.442721	4.411346	4.430171
170.00	5.653802	5.151800	5.220825	5.402801	4.693722	4.781573	4.969824	4.950999	4.976099
160.00	6.344055	5.816953	5.898528	6.036579	5.333776	5.421626	5.660077	5.653802	5.603602
150.00	6.990383	6.469556	6.532306	6.726832	6.049129	6.111879	6.362880	6.350330	6.187180
140.00	7.417085	6.921358	6.959008	7.184909	6.563681	6.613882	6.908808	6.877433	6.576231
130.00	7.517486	7.053134	7.053134	7.385710	6.827233	6.789582	7.109609	7.059409	6.651532
120.00	7.178634	6.714282	6.720557	7.071959	6.519756	6.488381	6.802133	6.745657	6.306405
110.00	6.450731	5.961279	6.011479	6.287580	5.710277	5.691452	5.948728	5.955003	5.622226
100.00	5.465551	5.001199	5.095324	5.170625	4.599597	4.643522	4.838048	4.907073	4.747521
90.00	4.436446	4.047394	4.166620	4.022294	3.520292	3.595592	3.739918	3.846593	3.874526
80.00	3.520292	3.275566	3.394791	3.005739	2.641788	2.735913	2.861414	2.980639	3.173856
70.00	2.880239	2.817488	2.905339	2.346861	2.171160	2.265286	2.390786	2.484912	2.779859
60.00	2.641788	2.729638	2.779838	2.177435	2.164885	2.233911	2.403336	2.453537	2.744766
50.00	2.773563	2.936714	2.968089	2.397061	2.466087	2.491187	2.673163	2.710813	3.021198
40.00	3.181440	3.432441	3.432441	2.754738	2.942989	2.917889	3.193990	3.193990	3.602080
30.00	3.815218	4.160345	4.122695	3.419891	3.733643	3.633242	4.016019	3.984644	4.359798
20.00	4.467821	4.863148	4.812948	4.147795	4.543122	4.417621	4.881973	4.831773	5.115158
10.00	4.900798	5.314950	5.252200	4.693722	5.120424	4.963549	5.471826	5.402801	5.588827
0.00	4.950999	5.346326	5.271025	4.825498	5.239650	5.095324	5.572227	5.496926	5.649014

Table S 3: Calculated relative energies of the rotation about the C1-O1 linkage in axial 2-methoxythiane. All energies are in kcal mol^{-1}.

ϕ	B3LYP-DZ	B3LYP-ADZ	B3LYP-ATZ	M062X-DZ	M062X-ADZ	M062X-ATZ	MP2-DZ	MP2-TZ	CCSD-DZ	PBE-ATZ
0.00	6.726832	6.287580	6.331505	6.457006	6.067954	6.017754	7.322960	6.664082	7.046859	6.149529
10.00	5.835778	5.484376	5.509476	5.559677	5.283575	5.233375	6.312680	5.741652	6.086779	5.327500
20.00	4.662347	4.405071	4.417621	4.336046	4.160345	4.097595	4.969824	4.492921	4.812948	4.216820
30.00	3.363416	3.193990	3.206540	2.986914	2.905339	2.817488	3.495192	3.124965	3.407341	3.005739
40.00	2.070760	1.964084	1.989185	1.669158	1.644058	1.587583	2.083310	1.838584	2.058210	1.813484
50.00	0.972630	0.916154	0.947530	0.633778	0.665153	0.633778	0.941254	0.809479	0.953805	0.803204
60.00	0.238451	0.213351	0.238451	0.125501	0.075300	0.087850	0.225901	0.169426	0.244726	0.156876
70.00	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
80.00	0.276101	0.276101	0.251001	0.345127	0.332577	0.301201	0.338852	0.370227	0.282376	0.326302
90.00	0.991455	0.953805	0.909879	1.129505	1.060480	1.016555	1.179706	1.211081	1.047930	1.066755
100.00	1.970359	1.857409	1.813484	2.265286	2.095860	2.064485	2.259011	2.259011	2.045660	2.051935
110.00	2.905339	2.685713	2.648063	3.319491	3.030839	3.024564	3.263016	3.219090	2.974364	2.949264
120.00	3.564217	3.244191	3.200265	3.959544	3.583042	3.583042	3.953269	3.865418	3.608142	3.532842
130.00	3.865418	3.507742	3.457542	4.216820	3.790118	3.758743	4.241920	4.103870	3.859143	3.790118
140.00	3.909344	3.551667	3.482642	4.229370	3.796393	3.708543	4.235645	4.028569	3.840318	3.790119
150.00	3.890519	3.507742	3.432441	4.166620	3.702268	3.595592	4.135245	3.859143	3.758743	3.683443
160.00	3.997194	3.520292	3.501467	4.022294	3.488917	3.451266	4.066219	3.733643	3.714818	3.695993
170.00	4.260745	3.689718	3.746193	3.909344	3.263016	3.281841	4.066219	3.683443	3.758743	3.884244
180.00	4.775298	4.141520	4.248195	4.147795	3.401066	3.432441	4.417621	3.934444	4.141520	4.310946
190.00	5.704002	4.982374	5.101599	5.032574	4.166620	4.204270	5.396526	4.756473	5.120424	5.076499
200.00	7.015484	6.180905	6.287580	6.557406	5.540851	5.603602	7.021759	6.212280	6.695457	6.193455
210.00	8.515216	7.561411	7.649262	8.414815	7.285310	7.348060	8.960743	8.025763	8.565416	7.504936
220.00	9.845522	8.791317	8.854067	10.04004	8.835242	8.879167	10.70520	9.688646	10.22829	8.672091
230.00	10.55460	9.437645	9.487845	10.73030	9.462745	9.531771	11.57743	10.52322	11.08797	9.280769
240.00	10.46675	9.305869	9.412545	10.57970	9.224294	9.337245	11.55233	10.47930	11.05660	9.142719
250.00	9.864347	8.703467	8.860342	9.814147	8.565416	8.697192	10.97502	9.939648	10.46675	8.540316
260.00	8.985843	7.875163	8.082239	8.791317	7.573961	7.737112	10.03377	9.086243	9.538046	7.743387
270.00	8.019488	6.984108	7.222560	7.674362	6.507206	6.733107	9.010943	8.157539	8.540316	6.877433
280.00	7.247660	6.312680	6.538581	6.745657	5.666352	5.936178	8.176364	7.385710	7.743387	6.193455
290.00	6.758207	5.955003	6.143254	6.362880	5.396526	5.647527	7.699462	6.946458	7.304135	5.791853
300.00	6.551131	5.848328	5.998929	6.318955	5.478101	5.722827	7.498661	6.764482	7.147259	5.634977
310.00	6.569956	5.917353	6.061679	6.231105	5.459276	5.691452	7.391985	6.664082	7.084509	5.691452
320.00	6.733107	6.111879	6.262480	6.350330	5.622427	5.791853	7.448461	6.676632	7.172359	5.898528
330.00	6.996658	6.400531	6.544856	6.582506	5.892253	5.992654	7.636712	6.839783	7.385710	6.212280
340.00	7.210009	6.645257	6.758207	6.814683	6.193455	6.237380	7.824962	7.040584	7.580236	6.475831
350.00	7.184909	6.676632	6.751932	6.877433	6.362880	6.350330	7.818687	7.090784	7.542586	6.538581
360.00	6.726832	6.287580	6.331505	6.457006	6.067954	6.017754	7.322960	6.664082	7.046859	6.149529

Table S 4: Calculated relative energies of the rotation about the C1-O1 linkage in equatorial 2-methoxythiane. All energies are in kcal mol^{-1}.

ϕ	B3LYP-DZ	B3LYP-ADZ	B3LYP-ATZ	M062X-DZ	M062X-ADZ	M062X-ATZ	MP2-TZ	MP2-QZ	CCSD-DZ	PBE-ATZ
360.00	5.785578	5.760478	5.760478	5.427901	5.427901	5.308675	5.678902	5.678902	5.923628	5.813218
350.00	5.377701	5.327500	5.314950	5.057674	5.032574	4.907073	5.214550	5.214550	5.528301	5.214525
340.00	4.568222	4.486646	4.461546	4.279570	4.223095	4.085045	4.329771	4.323496	4.693722	4.323357
330.00	3.495192	3.375966	3.357141	3.181440	3.093590	2.980639	3.187715	3.168890	3.564217	3.197102
320.00	2.315486	2.183710	2.183710	2.033110	1.907609	1.807209	1.982909	1.964084	2.334311	2.030889
310.00	1.229906	1.104405	1.116955	0.997730	0.865954	0.815754	0.941255	0.922429	1.217356	0.974737
300.00	0.420427	0.338852	0.351402	0.301201	0.200801	0.175701	0.251001	0.232176	0.414152	0.246634
290.00	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.018825	0.000000
280.00	0.018825	0.075300	0.081575	0.131775	0.225901	0.213351	0.144326	0.200801	0.000000	0.114844
270.00	0.420427	0.514552	0.514552	0.608678	0.753004	0.778104	0.658878	0.753004	0.357677	0.665039
260.00	1.010280	1.104405	1.104405	1.305206	1.443257	1.499732	1.380507	1.493457	0.953805	1.321336
250.00	1.581308	1.650333	1.644058	1.995459	2.095860	2.158610	2.064485	2.177435	1.568757	1.932097
240.00	2.014285	2.070760	2.045660	2.484912	2.572762	2.585312	2.528837	2.629238	2.001735	2.349365
230.00	2.284111	2.328036	2.296661	2.735913	2.811213	2.773563	2.698263	2.786113	2.189985	2.616782
220.00	2.415887	2.440987	2.390786	2.761013	2.804938	2.735913	2.660613	2.729638	2.221361	2.704971
210.00	2.528837	2.491187	2.434712	2.748463	2.723363	2.673163	2.597862	2.641788	2.277836	2.739732
200.00	2.754738	2.604137	2.572762	2.880239	2.717088	2.704538	2.679438	2.698263	2.484912	2.823231
190.00	3.137515	2.867689	2.880239	3.150065	2.817488	2.823764	2.899064	2.899064	2.786113	3.109185
180.00	3.683443	3.332041	3.382241	3.532842	3.106140	3.124965	3.281841	3.275566	3.244191	3.581962
170.00	4.361146	3.978369	4.041119	4.122694	3.645792	3.639517	3.890519	3.871694	3.921894	4.210875
160.00	5.107874	4.712548	4.781573	4.831773	4.348596	4.348596	4.662347	4.637247	4.737648	4.891532
150.00	5.773028	5.402801	5.471826	5.534577	5.076499	5.070224	5.446726	5.415351	5.547127	5.548953
140.00	6.224830	5.911078	5.967554	6.067954	5.666352	5.641252	6.093054	6.055404	6.180905	6.008202
130.00	6.325230	6.080504	6.118154	6.275030	5.948728	5.911078	6.400531	6.369155	6.475831	6.135280
120.00	5.961279	5.773028	5.816953	5.948729	5.678902	5.641252	6.180905	6.155804	6.218555	5.801095
110.00	5.151800	4.988649	5.082774	5.013749	4.762748	4.806673	5.352601	5.352601	5.371426	5.015499
100.00	4.110145	3.972094	4.122695	3.808943	3.576767	3.658342	4.191720	4.223095	4.204270	4.042034
90.00	3.118690	3.018289	3.206540	2.635513	2.453537	2.553937	3.049665	3.099865	3.081040	3.075846
80.00	2.403336	2.365686	2.553937	1.832309	1.706808	1.832309	2.252736	2.309211	2.309211	2.374664
70.00	2.158610	2.171160	2.328036	1.618958	1.543657	1.662883	2.020560	2.064485	2.120960	2.140364
60.00	2.422162	2.447262	2.553937	1.989185	1.913884	2.008010	2.271561	2.277836	2.422162	2.372711
50.00	2.911614	2.930439	3.012014	2.397061	2.328036	2.378236	2.666888	2.666888	2.867689	2.861824
40.00	3.608142	3.626967	3.695993	3.005739	2.961814	2.968089	3.319491	3.325766	3.532842	3.561680
30.00	4.430171	4.455271	4.499197	3.834043	3.834043	3.796393	4.197995	4.204270	4.405071	4.374698
20.00	5.202000	5.220825	5.252200	4.674897	4.693722	4.630972	5.045124	5.057674	5.252200	5.168119
10.00	5.710277	5.710277	5.722827	5.264750	5.277300	5.195725	5.603602	5.609877	5.816953	5.666815
0.00	5.785578	5.760478	5.760478	5.427901	5.427901	5.308675	5.678902	5.678902	5.923628	5.741156

Table S 5: The ROMP2(CP2O)/aug-cc-pVTZ calculated potential energy of the rotation about the C1-O1 linkage in MTHP and MT. All energies are in kcal mol^{-1}.

MTHP			MT		
ϕ	axial	equatorial	ϕ	axial	equatorial
0.0	8.387	5.518	0.0	6.450	5.656
10.0	7.326	5.439	10.0	5.573	5.587
20.0	5.559	4.883	20.0	4.384	5.044
30.0	3.485	4.059	30.0	3.070	4.204
40.0	1.657	3.287	40.0	1.822	3.334
50.0	0.456	2.801	50.0	0.819	2.686
60.0	0.007	2.553	60.0	0.192	2.296
61.2	0.000		68.0	0.000	
64.3		2.526	70.0	0.032	2.088
70.0	0.196	2.604	70.8		2.065
80.0	0.838	3.093	80.0	0.402	2.325
90.0	1.747	3.939	90.0	1.229	3.097
100.0	2.695	4.973	100.0	2.259	4.193
110.0	3.481	5.997	110.0	3.189	5.303
120.0	3.960	6.771	120.0	3.803	6.090
130.0	4.094	7.077	130.0	4.019	6.310
140.0	3.982	6.903	140.0	3.935	6.012
150.0	3.834	6.390	150.0	3.772	5.386
159.7	3.796		160.0	3.653	4.616
160.0	3.797	5.703	169.2	3.589	
170.0	3.884	5.008	170.0	3.614	3.867
180.0	4.179	4.461	180.0	3.856	3.275
190.0	4.817	4.144	190.0	4.646	2.902
200.0	5.836	4.024	200.0	6.043	2.701
202.6		4.018	208.6		2.624
210.0	7.085	4.055	210.0	7.775	2.644
220.0	8.262	4.164	220.0	9.345	2.722
230.0	9.004	4.169	230.0	10.143	2.777
240.0	9.025	3.902	240.0	10.080	2.617
250.0	8.829	3.304	250.0	9.538	2.164
259.8	8.738		260.0	8.705	1.483
260.0	8.738	2.439	270.0	7.804	0.755
270.0	8.819	1.466	280.0	7.060	0.213
280.0	9.002	0.605	290.0	6.625	0.020
290.0	9.177	0.081	290.0		0.000
295.5		0.000	300.0	6.437	0.260
300.0	9.294	0.061	310.0	6.344	0.948
310.0	9.394	0.616	312.9	6.315	
320.0	9.475	1.651	320.0	6.375	1.990
330.0	9.496	2.921	330.0	6.547	3.187
340.0	9.385	4.140	340.0	6.768	4.323
350.0	9.049	5.061	350.0	6.844	5.202
360.0	8.387	5.518	360.0	6.450	5.656

Table S 6: The ROMP2/aug-cc-pVTZ EDA contributions to the interaction energy between the six-membered ring and the methoxy group according the CP2O fragmentation scheme for MTHP and MT in vacuum. All energies are in kcal mol^{-1}.

Method	AGT	ATG	AGG	EGT	ETG	EGG
			MT			
ΔE^{ele}	-171.43	-164.77	-165.23	-168.27	-162.49	-166.71
ΔE^{ex}	-289.20	-283.06	-285.17	-281.58	-274.82	-281.72
ΔE^{rep}	649.27	634.60	639.26	636.54	619.66	638.51
ΔE^{pol}	-251.66	-245.93	-245.90	-251.88	-244.46	-252.73
ΔE^{disp}	-43.55	-43.01	-44.15	-44.18	-43.57	-44.87
ΔE_{HF}	-63.02	-59.16	-57.04	-65.18	-62.10	-62.65
ΔE_{MP2}	-106.57	-102.17	-101.18	-109.36	-105.67	-107.52
			MTHP			
ΔE^{ele}	-180.34	-172.97	-173.23	-179.01	-170.61	-177.24
ΔE^{ex}	-293.02	-285.42	-291.10	-288.62	-279.12	-287.54
ΔE^{rep}	664.81	644.99	661.94	661.29	635.43	660.32
ΔE^{pol}	-260.15	-251.17	-258.05	-265.99	-253.17	-265.05
ΔE^{disp}	-41.67	-41.46	-42.69	-42.02	-42.29	-42.52
ΔE_{HF}	-68.69	-64.58	-60.44	-72.33	-67.47	-69.51
ΔE_{MP2}	-110.36	-106.04	-103.13	-114.35	-109.75	-112.03

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