Supporting Information for Improved modeling of anharmonicity for furan microsolvation

Wassja A. Kopp[†], Matthias Mödden[†], Narasimhan Viswanathan[†], Gabriel Rath[†], and Kai Leonhard[†,⋆]

[†]Chair of Technical Thermodynamics, RWTH Aachen University, 52062 Aachen, Germany
⋆to whom correspondence should be addressed, email: kai.leonhard@ltt.rwth-aachen.de

March 22, 2023

Abstract

This is Supplementary material for "The TamkinTools article" in PCCP. It contains all structures, energies, and hindered rotor treatments employed. Furthermore, the code[1] that was used is given in TAMkinTools.zip. All input and output files for the TAMkin / TAMkinTools calculations are given in SI.zip. Therein, the folder final_data_original contains the scans as used by TAMkin; the folder final_data_improved contains the scans as improved with TAMkinTools. In each of these folders, there are folders for furan (Fu), 2-methylfuran (2mFu), and 2,5-methylfuran (25dmFu). Therein again, two folders OH and PI distinguish the two possible bonding sites.

Contents

[1]also available at https://git.rwth-aachen.de/Wassja.Kopp/tamkintools/-/releases/1_0PCCP

S1 Geometries employed in this study

S1.1 Methanol – furan system

S1.1.1 Furan OH top Ot

up to table of contents

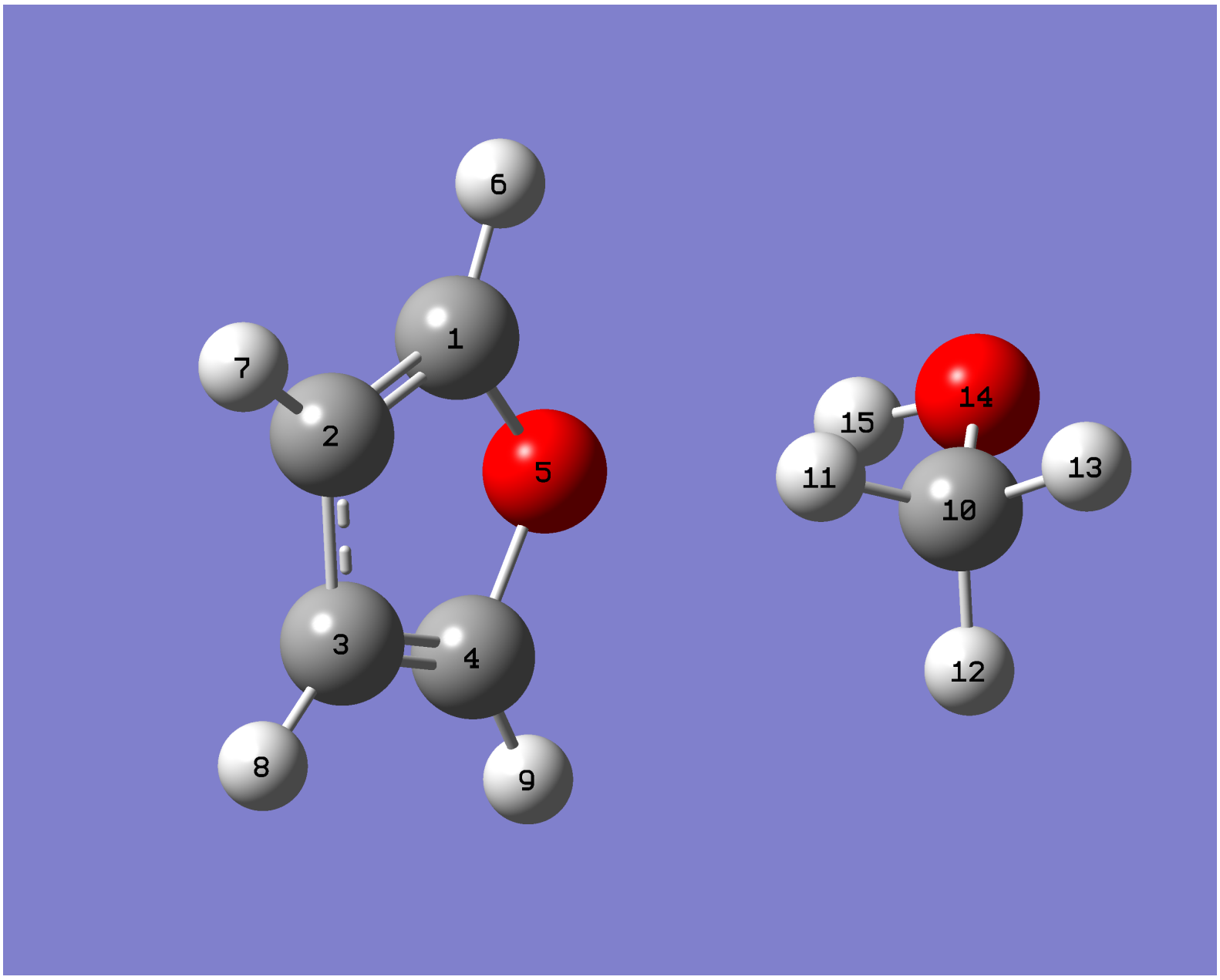

Figure S1: OH-bonded methanol – furan structure in top conformation Ot.

Table S1: Methanol – furan Ot

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-0.8635090	1.1517500	-0.1031540
2	C	1			1.3596776			-1.7742830	0.6171140	0.7532210
3	C	2	1		1.4363885	106.3125829		-1.8884780	-0.7717980	0.4052340
4	C	3	2	1	1.3597057	106.2695006	0.0573672	-1.0371800	-0.9750300	-0.6353370
5	O	4	3	2	1.3682976	110.2553260	-0.0387796	-0.4003660	0.1913940	-0.9611610
6	H	1	2	3	1.0760892	134.0561603	-179.3651624	-0.4435310	2.1341910	-0.2312010
7	H	2	1	5	1.0777065	126.2291097	-179.8855113	-2.3012420	1.1430600	1.5324170
8	H	3	2	1	1.0777017	127.4726825	-179.8054212	-2.5197890	-1.5135200	0.8664670
9	H	4	3	2	1.0761335	133.9381110	-179.6751127	-0.7786600	-1.8324090	-1.2321050
10	C	5	4	3	3.2983852	95.5746401	96.0746128	2.3147590	-0.4206530	0.8088220
11	H	10	5	4	1.0956086	62.1003251	-77.4750056	1.4189490	-0.0858340	1.3434050
12	H	10	5	4	1.0959491	91.5422564	32.9613275	2.2305550	-1.4970550	0.6207450
13	H	10	5	4	1.0895244	159.9942721	-143.9404426	3.1830950	-0.2488100	1.4440590
14	O	10	5	4	1.4213518	64.6892012	146.6427033	2.5235430	0.3143430	-0.3896900
15	H	14	10	5	0.9617644	107.2251881	-13.2707409	1.7173490	0.2461880	-0.9096870

S1.1.2 Furan OH planar Op

up to table of contents

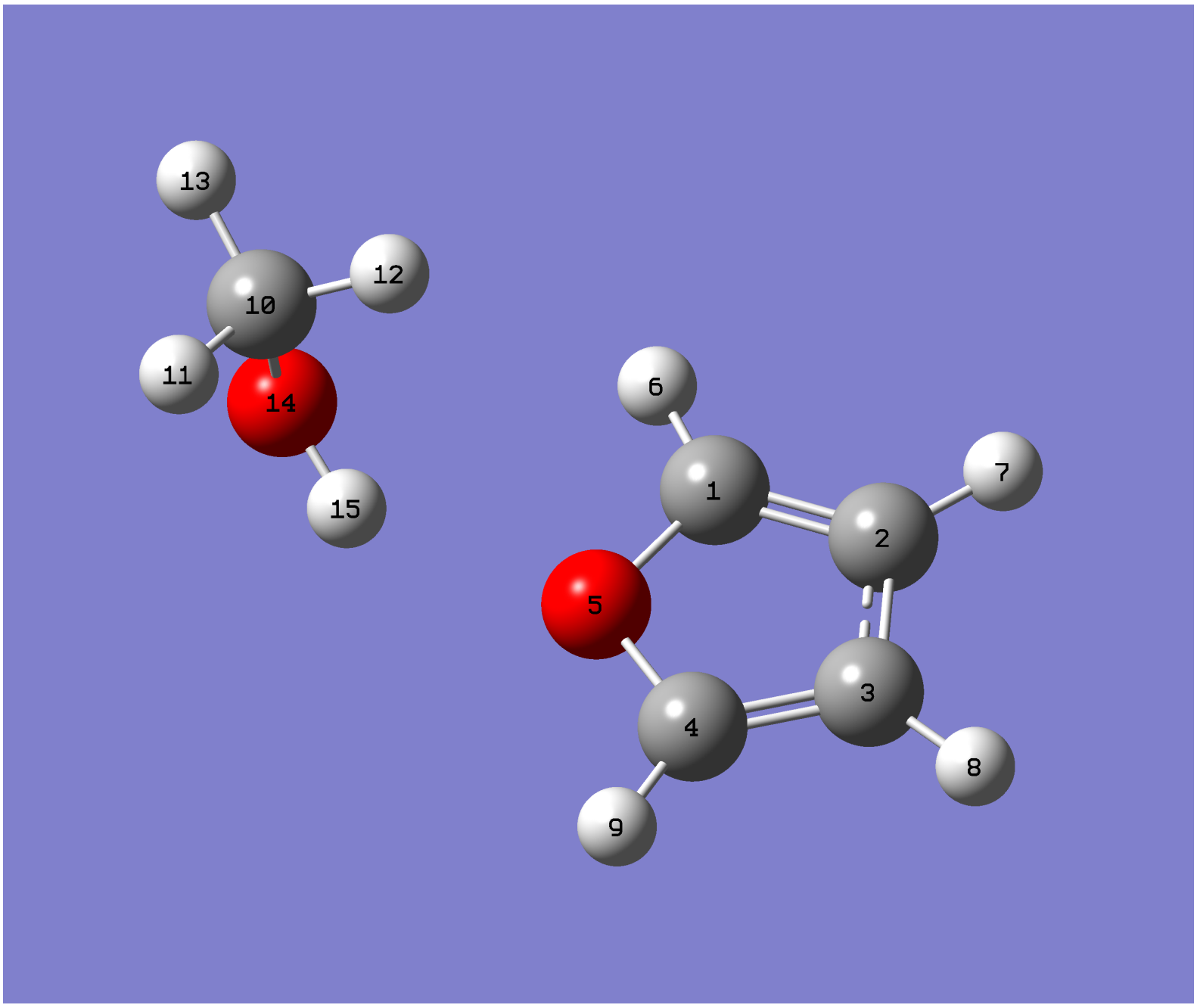

Figure S2: OH-bonded methanol – furan structure in plane conformation Op.

Table S2: Methanol – furan Op

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							0.6586580	0.9109110	-0.1866770
2	C	1			1.3595904			1.9692160	1.0180380	0.1589350
3	C	2	1		1.4365992	106.3692336		2.4744270	-0.3235900	0.2517430
4	C	3	2	1	1.3597438	106.2800379	-0.0028897	1.4319830	-1.1448020	-0.0446090
5	O	4	3	2	1.3674764	110.1929740	-0.0446830	0.3123020	-0.4076320	-0.3145840
6	H	1	2	3	1.0764165	134.5587054	-179.7625615	-0.1325150	1.6157740	-0.3761130
7	H	2	1	5	1.0776621	126.2042714	179.9607813	2.5106240	1.9347610	0.3258240
8	H	3	2	1	1.0777083	127.4750326	179.9783184	3.4760230	-0.6310720	0.5041620
9	H	4	3	2	1.0760065	133.9335471	179.9598544	1.3171500	-2.2128790	-0.1063730
10	C	5	4	3	3.4174466	140.7882001	-124.6747508	-2.9377940	-0.0661630	0.6850240
11	H	10	5	4	1.0956135	100.5419703	-35.3866601	-3.1896730	-1.1089450	0.9075810
12	H	10	5	4	1.0958078	62.7665373	70.3406292	-2.1609300	0.2644690	1.3835650
13	H	10	5	4	1.0894304	150.9042948	149.5767514	-3.8270470	0.5438430	0.8398800
14	O	10	5	4	1.4211436	57.9644445	-144.8373978	-2.5431930	0.1088320	-0.6689760
15	H	14	10	5	0.9622023	107.4270044	23.9557337	-1.7254390	-0.3819210	-0.7965420

S1.1.3 Furan OH-bonded OhiTS

up to table of contents

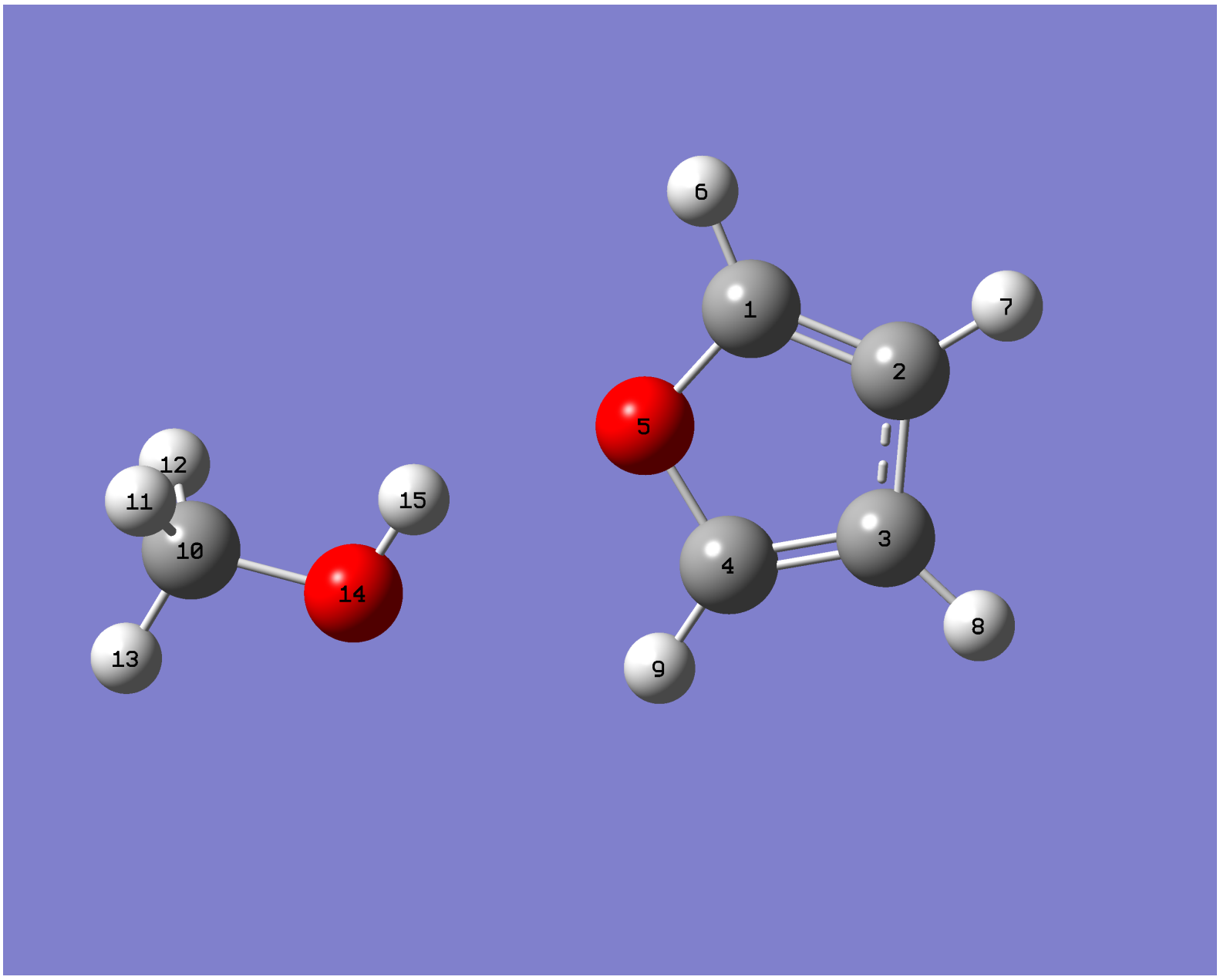

Figure S3: OH-bonded methanol – furan transition state structure of highest energy.

Table S3: OH-bonded methanol – furan transition state of highest energy OhiTS

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							1.5451280	1.1693480	0.0000080
2	C	1			1.3597363			2.6484850	0.3746870	-0.0000090
3	C	2	1		1.4367073	106.2625998		2.1689110	-0.9796160	-0.0000150
4	C	3	2	1	1.3595814	106.4020587	0.0000000	0.8113160	-0.9061490	-0.0000010
5	O	1	2	3	1.3673152	110.1919615	0.0000000	0.4121840	0.4038490	0.0000130
6	H	1	2	3	1.0760020	133.8948247	180.0000000	1.3929120	2.2345290	0.0000180
7	H	2	1	5	1.0777374	126.2418613	180.0000000	3.6734980	0.7076530	-0.0000170
8	H	3	2	1	1.0776441	127.4200779	-180.0000000	2.7571040	-1.8825810	-0.0000270
9	H	4	3	2	1.0764615	134.6885141	180.0000000	0.0140440	-1.6294240	0.0000010
10	C	5	1	2	4.0344156	148.3486649	-179.9986492	-3.6187090	0.2352940	0.0000010
11	H	10	5	1	1.0956672	95.6774585	-54.8559075	-3.7532310	0.8578380	0.8915330
12	H	10	5	1	1.0956664	95.6775069	54.8538294	-3.7532270	0.8578490	-0.8915230
13	H	10	5	1	1.0893360	137.3065525	179.9990436	-4.3878030	-0.5361640	-0.0000050
14	O	10	5	1	1.4201336	30.2877700	179.9989525	-2.3635660	-0.4290820	0.0000000
15	H	14	10	5	0.9623740	108.8198514	0.0000000	-1.6630250	0.2307710	0.0000060

S1.1.4 Furan OH-bonded OloTS

up to table of contents

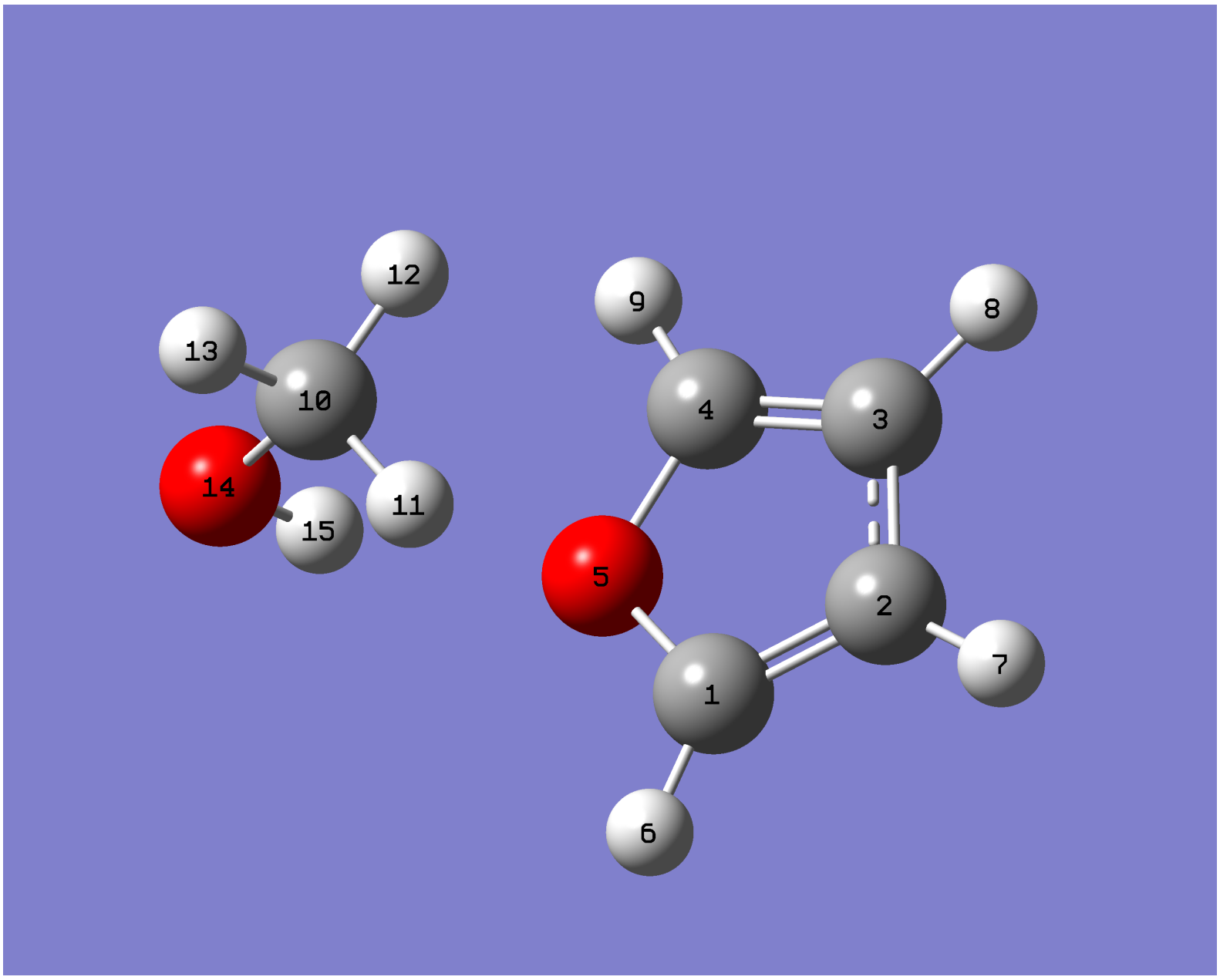

Figure S4: OH-bonded methanol – furan transition state structure of lowest energy.

Table S4: OH-bonded methanol – furan transition state of lowest energy OloTS

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							0.9637520	-1.0999170	-0.3666400
2	C	1			1.3595240			1.8863770	-0.7182480	0.5560720
3	C	2	1		1.4364970	106.3041531		1.8863770	0.7182490	0.5560700
4	C	3	2	1	1.3595235	106.3041850	0.0000000	0.9637520	1.0999160	-0.3666420
5	O	4	3	2	1.3687503	110.2213379	0.0413680	0.3870760	-0.0000010	-0.9420590
6	H	1	2	3	1.0761581	134.0280575	179.9592771	0.6101510	-2.0525320	-0.7210510
7	H	2	1	5	1.0776950	126.2477947	-179.8269790	2.4936390	-1.3735250	1.1587920
8	H	3	2	1	1.0776956	127.4475906	-179.7821565	2.4936400	1.3735270	1.1587890
9	H	4	3	2	1.0761587	134.0280432	-179.9591852	0.6101520	2.0525310	-0.7210560
10	C	5	4	3	3.3272674	96.6957687	99.0535287	-2.3789590	0.0000020	0.9072000
11	H	10	5	4	1.0958838	76.5140474	-110.6384616	-1.8407110	-0.8899680	1.2524590
12	H	10	5	4	1.0958838	76.5141933	2.6205137	-1.8407150	0.8899760	1.2524550
13	H	10	5	4	1.0895126	170.6322886	125.9914717	-3.3711810	0.0000010	1.3572370
14	O	10	5	4	1.4206486	63.6158715	125.9909449	-2.5614640	-0.0000010	-0.5016770
15	H	14	10	5	0.9620137	107.3467226	0.0000000	-1.6876610	-0.0000010	-0.9040930

S1.1.5 Furan transition state between OH and pi-bonded conformation TS

up to table of contents

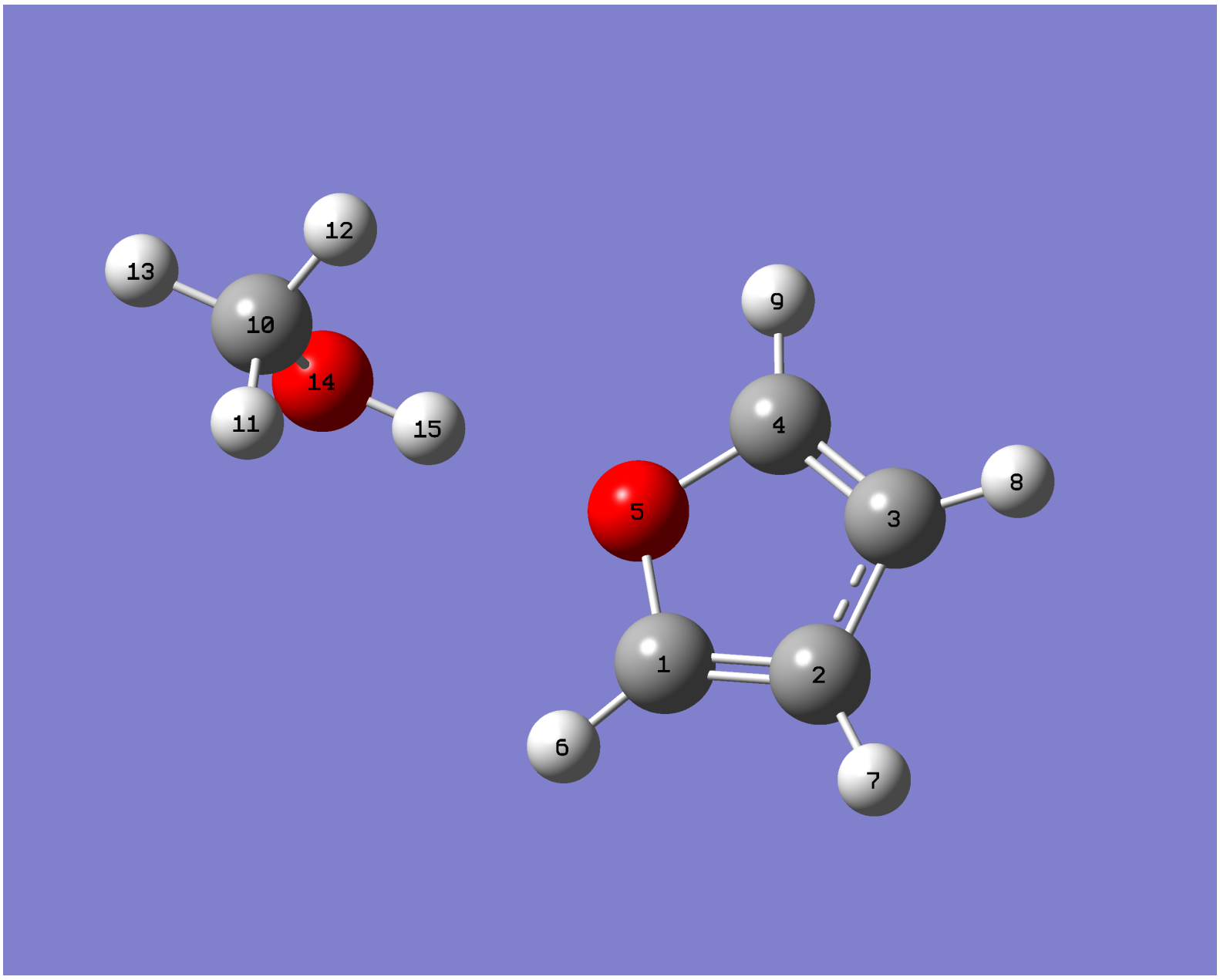

Figure S5: Methanol – furan transition state between OH- and pi-bonded conformation.

Table S5: Methanol – furan transition state between OH- and pi-bonded conformation.

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							0.3546530	-1.0128590	-1.1004770
2	C	1			1.3593363			0.3546530	-2.3173720	-0.7183240
3	C	2	1		1.4366480	106.3277810		0.3546530	-2.3173720	0.7183240
4	C	3	2	1	1.3593363	106.3277810	0.0000000	0.3546530	-1.0128590	1.1004770
5	O	1	2	3	1.3683667	110.1365661	-0.0345186	0.3538790	-0.1996080	0.0000000
6	H	1	2	3	1.0760830	134.0871415	179.7835461	0.3575730	-0.5116620	-2.0527100
7	H	2	1	5	1.0776285	126.2287648	-179.9665639	0.3556840	-3.1729590	-1.3734980
8	H	3	2	1	1.0776285	127.4434149	-179.9309574	0.3556840	-3.1729590	1.3734980
9	H	4	3	2	1.0760830	134.0871415	-179.7835461	0.3575730	-0.5116620	2.0527100
10	C	5	1	2	3.4501758	121.0084030	-144.3681922	-1.3693680	2.7893940	0.0000000
11	H	10	5	1	1.0961556	79.7128220	14.1480271	-1.7991700	2.3156440	-0.8901620
12	H	10	5	1	1.0961556	79.7128220	125.3947235	-1.7991700	2.3156440	0.8901620
13	H	10	5	1	1.0896072	165.1126605	-110.2286247	-1.6528000	3.8414920	0.0000000
14	O	10	5	1	1.4193660	57.9857394	-110.2286247	0.0490900	2.7386320	0.0000000
15	H	14	10	5	0.9626969	107.4906692	0.0000000	0.3054060	1.8106840	0.0000000

S1.1.6 Furan π-bonded conformation PI

up to table of contents

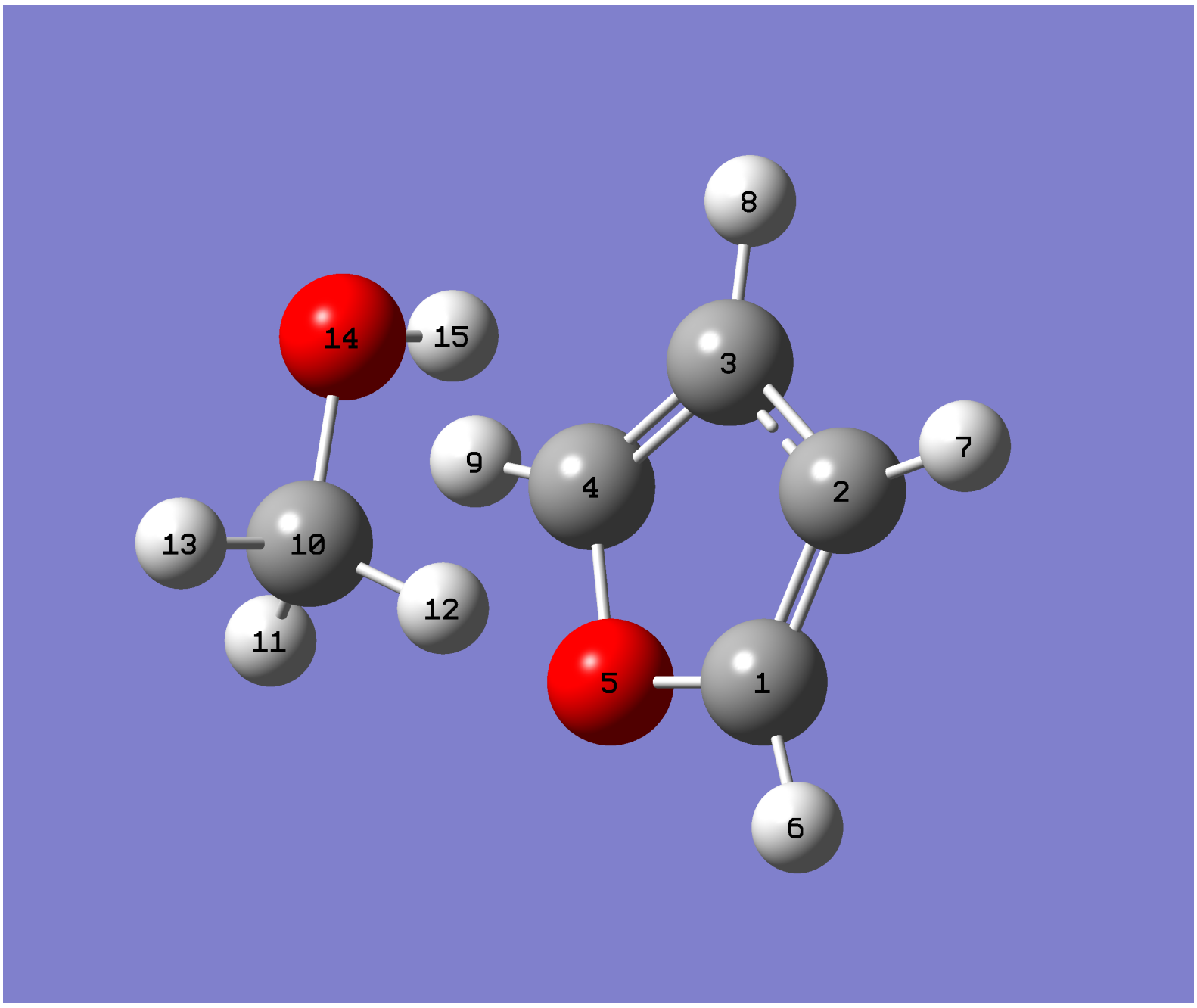

Figure S6: π-bonded methanol – furan structure.

Table S6: π-bonded methanol – furan structure.

#	N	ref atom A	B	C	Bond	Angle	Dihedral	X	Y	Z
1	C							1.1681400	-1.0520670	0.4836110
2	C	1			1.3613521			1.2589270	0.1285170	1.1553690
3	C	2	1		1.4367598	106.0933364		1.1776490	1.1607790	0.1593230
4	C	3	2	1	1.3633249	106.1102765	0.0945681	1.0418100	0.5219240	-1.0373670
5	O	4	3	2	1.3629689	110.3554653	0.0264895	1.0324530	-0.8288020	-0.8553340
6	H	1	2	3	1.0760956	133.7496311	-179.9082736	1.1780010	-2.0841420	0.7880870
7	H	2	1	5	1.0776579	126.4361433	179.9697805	1.3716430	0.2521430	2.2199620
8	H	3	2	1	1.0781321	127.5494588	-179.2315472	1.2251550	2.2269090	0.3125510
9	H	4	3	2	1.0762235	133.7097082	179.9458647	0.9435610	0.8605190	-2.0542040
10	C	5	4	3	3.5588973	88.6206819	81.5718959	-2.4132430	-0.6024260	0.0058760
11	H	10	5	4	1.0952793	50.3190218	108.8505031	-1.9424990	-1.0183360	-0.8913730
12	H	10	5	4	1.0955967	80.0913842	-126.4869347	-2.0345570	-1.1388290	0.8829170
13	H	10	5	4	1.0894991	158.7585546	117.1361366	-3.4891070	-0.7608800	-0.0605870
14	O	10	5	4	1.4213835	86.5804169	-13.5882735	-2.2067380	0.7997780	0.1131640
15	H	14	10	5	0.9619970	107.6971223	-14.5821229	-1.2576110	0.9544440	0.1391360

S1.1.7 Furan π-bonded low TS PiloTS

up to table of contents

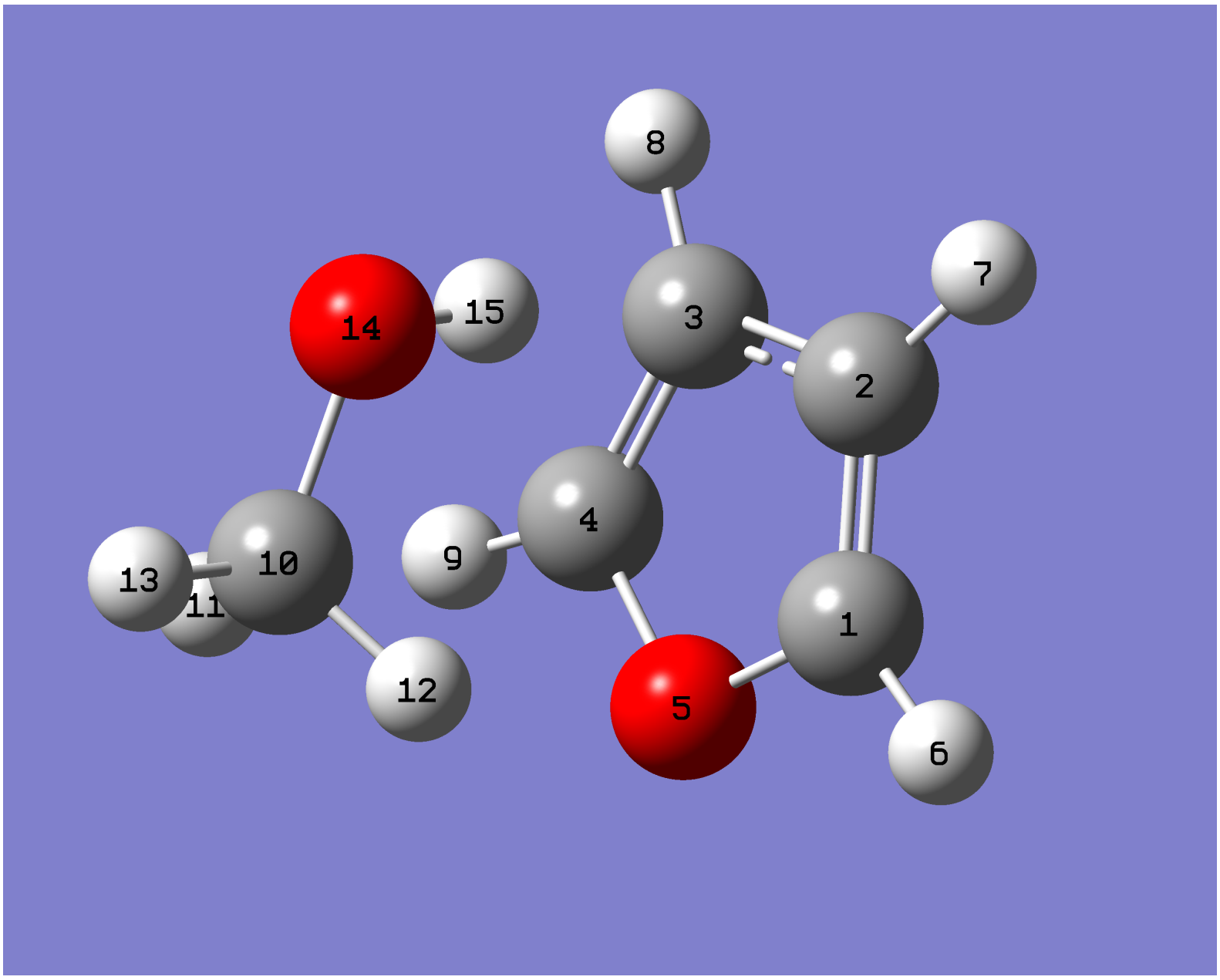

Figure S7: π-bonded methanol – furan transition state of lowest energy.

Table S7: π-bonded methanol – furan transition state of lowest energy.

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							1.1249970	-0.3699930	1.0960270
2	C	1			1.3624785			1.1490690	0.9389380	0.7185780
3	C	2	1		1.4373030	106.0786341		1.1490730	0.9388260	-0.7187250
4	C	3	2	1	1.3624786	106.0786266	0.0000000	1.1250040	-0.3701640	-1.0959700
5	O	1	2	3	1.3630754	110.4015296	0.0066087	1.1102470	-1.1803530	0.0000920
6	H	1	2	3	1.0761103	133.6909676	179.9533050	1.1164580	-0.8686090	2.0496110
7	H	2	1	5	1.0779151	126.3521864	-179.5799579	1.1710390	1.7930980	1.3757150
8	H	3	2	1	1.0779154	127.5677121	-179.5800922	1.1710440	1.7928840	-1.3759950
9	H	4	3	2	1.0761106	133.6909152	-179.9533539	1.1164700	-0.8689280	-2.0494770
10	C	5	1	2	3.5478124	85.1284915	-83.3909127	-2.3913740	-0.6097190	0.0000050
11	H	10	5	1	1.0955564	62.5062423	167.4486250	-1.9548780	-1.0758600	-0.8901790
12	H	10	5	1	1.0955568	62.5038201	-59.8530341	-1.9548770	-1.0758390	0.8902000
13	H	10	5	1	1.0894400	160.7546016	-126.1981023	-3.4642970	-0.7987050	0.0000080
14	O	10	5	1	1.4205703	92.2787175	53.7980250	-2.2188160	0.8003320	-0.0000120
15	H	14	10	5	0.9617409	107.4289964	0.0009763	-1.2730330	0.9748030	-0.0000090

S1.1.8 Furan π-bonded high TS PihiTS

up to table of contents

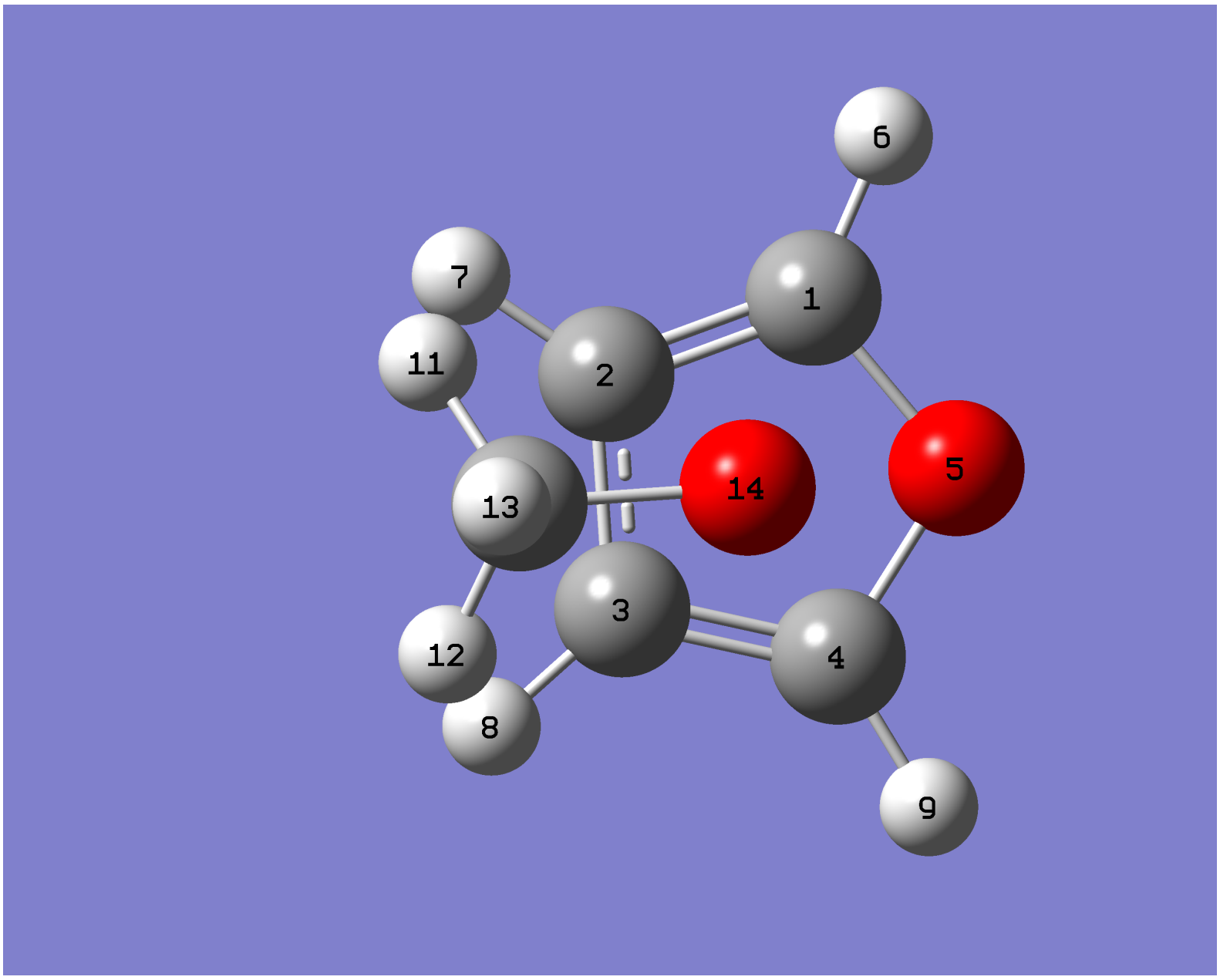

Figure S8: π-bonded methanol – furan transition state of highest energy.

Table S8: π-bonded methanol – furan transition state of highest energy.

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-1.3988190	1.0962610	-0.1636310
2	C	1			1.3623181			-0.7388580	0.7184740	0.9666960
3	C	2	1		1.4369410	106.1000269		-0.7388570	-0.7184670	0.9667010
4	C	3	2	1	1.3623186	106.1000304	0.0000000	-1.3988190	-1.0962630	-0.1636230
5	O	1	2	3	1.3633775	110.3786886	-0.0360477	-1.8068210	-0.0000030	-0.8640150
6	H	1	2	3	1.0760463	133.7396491	-179.7277782	-1.6473290	2.0495020	-0.5965860
7	H	2	1	5	1.0778149	126.3273113	-179.7299278	-0.3121380	1.3756810	1.7067460
8	H	3	2	1	1.0778142	127.5719416	-179.6887450	-0.3121380	-1.3756690	1.7067550
9	H	4	3	2	1.0760457	133.7397434	179.7277962	-1.6473290	-2.0495060	-0.5965720
10	C	3	2	1	3.7106801	78.8357853	109.1581720	2.8332410	0.0000010	0.2645140
11	H	10	3	2	1.0960485	82.9401057	30.7416165	2.6331900	0.8911190	0.8704930
12	H	10	3	2	1.0960489	64.0398513	145.6516431	2.6331910	-0.8911130	0.8705000
13	H	10	3	2	1.0894461	168.2950173	-162.2854361	3.8872190	0.0000000	-0.0112090
14	O	10	3	2	1.4191961	69.9174774	-85.8622579	2.0894290	-0.0000030	-0.9441470
15	H	14	10	3	0.9615428	107.4387918	11.8971771	1.1571400	-0.0000030	-0.7087710

S1.2 Methanol – 2-methylfuran system

S1.2.1 2-methylfuran OH top Ot

up to table of contents

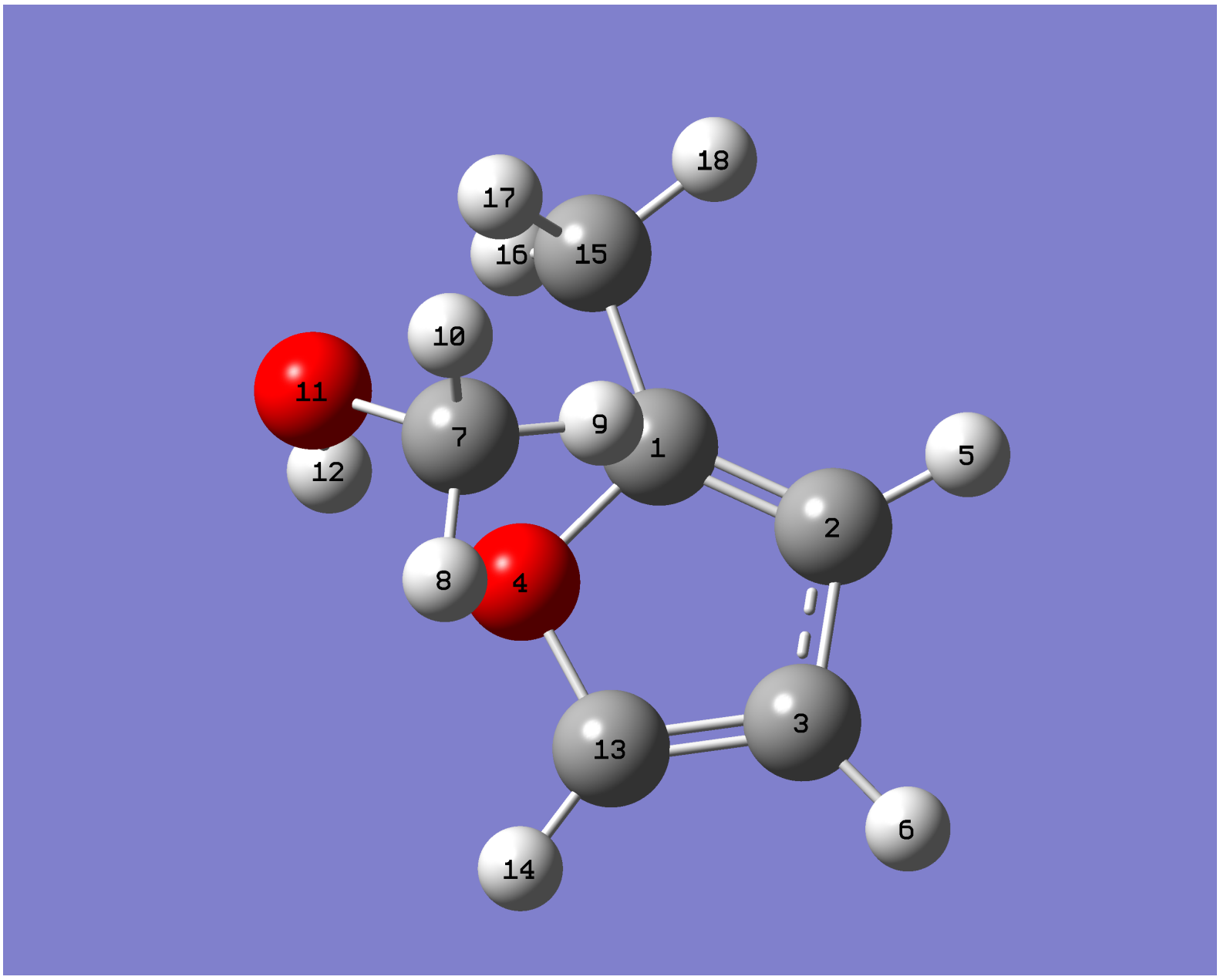

Figure S9: OH-bonded methanol – 2-methylfuran structure in top conformation Ot.

Table S9: Methanol – 2-methylfuran Ot

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							0.8233210	0.7861660	0.0135940
2	C	1			1.3628783			1.6966520	0.1481510	0.8428510
3	C	2	1		1.4369167	106.9706862		1.8220460	-1.2003180	0.3626040
4	O	1	2	3	1.3755721	109.2580843	0.0288484	0.3966330	-0.0902520	-0.9569870
5	H	2	1	4	1.0781380	125.7320405	179.8406558	2.1935970	0.5878750	1.6925980
6	H	3	2	1	1.0779235	127.5327192	179.8017802	2.4315270	-1.9893350	0.7723650
7	C	4	1	2	3.3047572	90.4895049	96.8646438	-2.3327060	-0.7398750	0.7894720
8	H	7	4	1	1.0954943	94.1741487	-139.8394549	-2.3166860	-1.8123150	0.5664840
9	H	7	4	1	1.0956836	61.0104214	-30.7537647	-1.4114730	-0.4780310	1.3217220
10	H	7	4	1	1.0895384	157.3104673	37.1506473	-3.1820150	-0.5350860	1.4404940
11	O	7	4	1	1.4223350	63.7663653	107.6986532	-2.5088840	0.0447850	-0.3836890
12	H	11	7	4	0.9623241	107.1915715	16.6592968	-1.7174630	-0.0641100	-0.9202170
13	C	3	2	1	1.3583019	106.2390999	-0.0045850	1.0161250	-1.2919920	-0.7269240
14	H	13	3	2	1.0762071	134.0583954	179.5492588	0.7806590	-2.0815260	-1.4193210
15	C	1	2	3	1.4858498	134.1919629	179.6301195	0.2655240	2.1621990	-0.0424890
16	H	15	1	2	1.0931300	111.0439109	119.3280353	0.5310440	2.6554240	-0.9811910
17	H	15	1	2	1.0928293	110.8596186	-120.4426631	-0.8243550	2.1437720	0.0356140
18	H	15	1	2	1.0901392	109.4697706	-0.3775280	0.6674000	2.7510700	0.7822110

S1.2.2 2-methylfuran OH transition state OloTS

up to table of contents

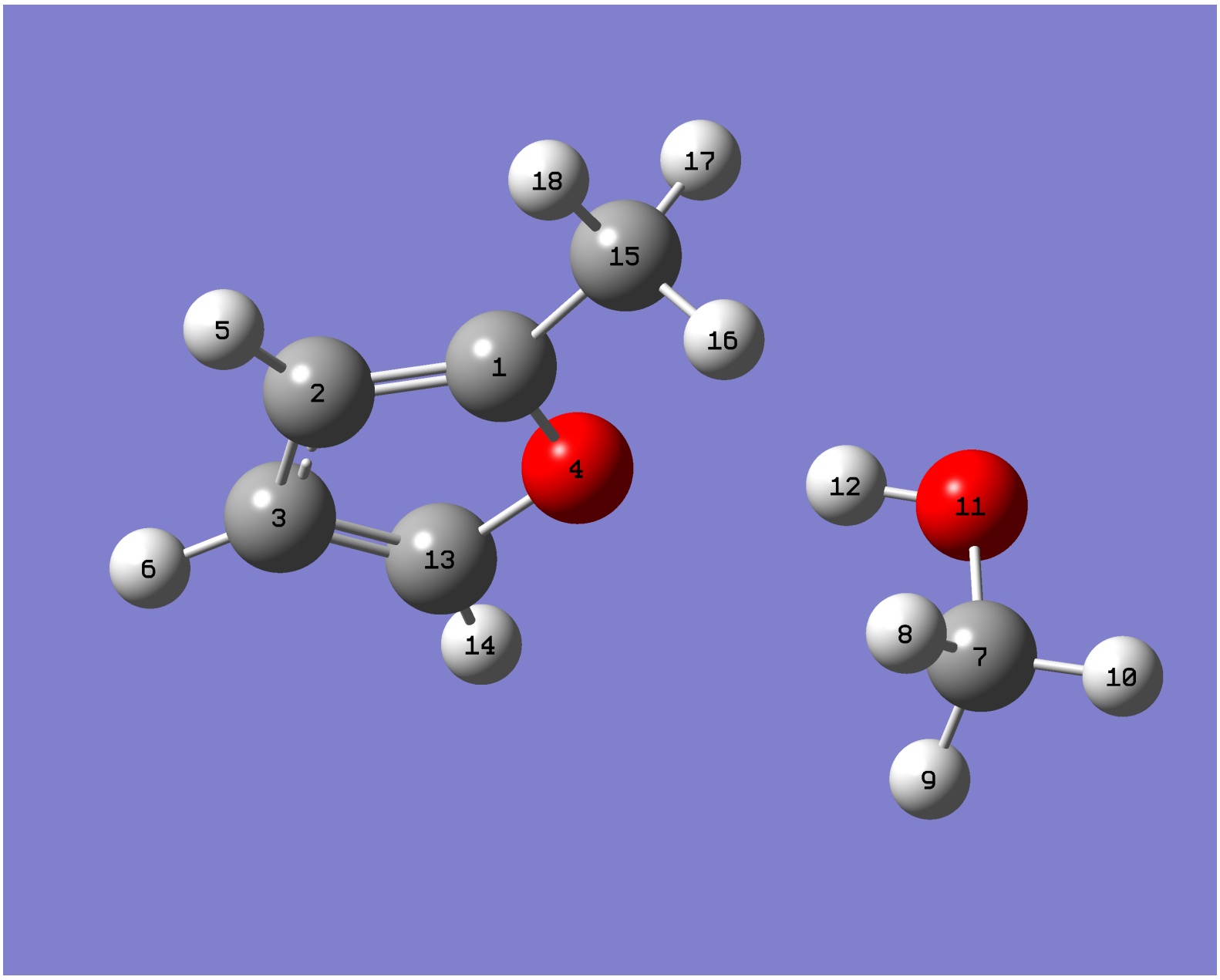

Figure S10: OH-bonded methanol – 2-methylfuran transition state with lowest energy.

Table S10: OH-bonded methanol – 2-methylfuran transition state with lowest energy.

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-0.9461110	0.7494900	-0.0203550
2	C	1			1.3622866			-2.2221310	0.4263350	0.3305990
3	C	2	1		1.4372750	106.9772756		-2.3453260	-0.9995680	0.1987540
4	O	1	2	3	1.3751583	109.1880279	-0.0070532	-0.2677090	-0.3964510	-0.3633570
5	H	2	1	4	1.0780436	125.7470190	-179.9246844	-2.9842050	1.1212870	0.6443870
6	H	3	2	1	1.0778415	127.5042114	-179.9071192	-3.2170060	-1.6035240	0.3915060
7	C	4	1	2	3.4262627	112.9588024	-141.4009385	2.9843420	-0.3978860	0.7152710
8	H	7	4	1	1.0967123	74.0191969	25.0316734	2.4428990	0.2766800	1.3894950
9	H	7	4	1	1.0960157	85.5241468	135.7242486	2.7903270	-1.4305210	1.0271580
10	H	7	4	1	1.0896569	163.5380330	-75.7328755	4.0513210	-0.2020490	0.8180130
11	O	7	4	1	1.4187508	58.1465759	-104.6896214	2.6467680	-0.1777500	-0.6450370
12	H	11	7	4	0.9632075	107.3816102	-6.9948877	1.7000380	-0.3306770	-0.7349500
13	C	3	2	1	1.3578738	106.2906457	-0.0243331	-1.1357930	-1.4488880	-0.2242860
14	H	13	3	2	1.0760655	134.1682389	-179.7959248	-0.7385850	-2.4198110	-0.4639760
15	C	1	2	3	1.4859332	134.2164211	179.8203521	-0.1855560	2.0232480	-0.1045810
16	H	15	1	2	1.0927529	111.3553971	119.3203784	0.6780090	2.0161040	0.5649810
17	H	15	1	2	1.0926210	111.2025117	-120.6344409	0.1829430	2.1971700	-1.1183760
18	H	15	1	2	1.0900487	109.4338034	-0.6537383	-0.8347510	2.8525560	0.1764890

S1.2.3 2-methylfuran OH planar Op

up to table of contents

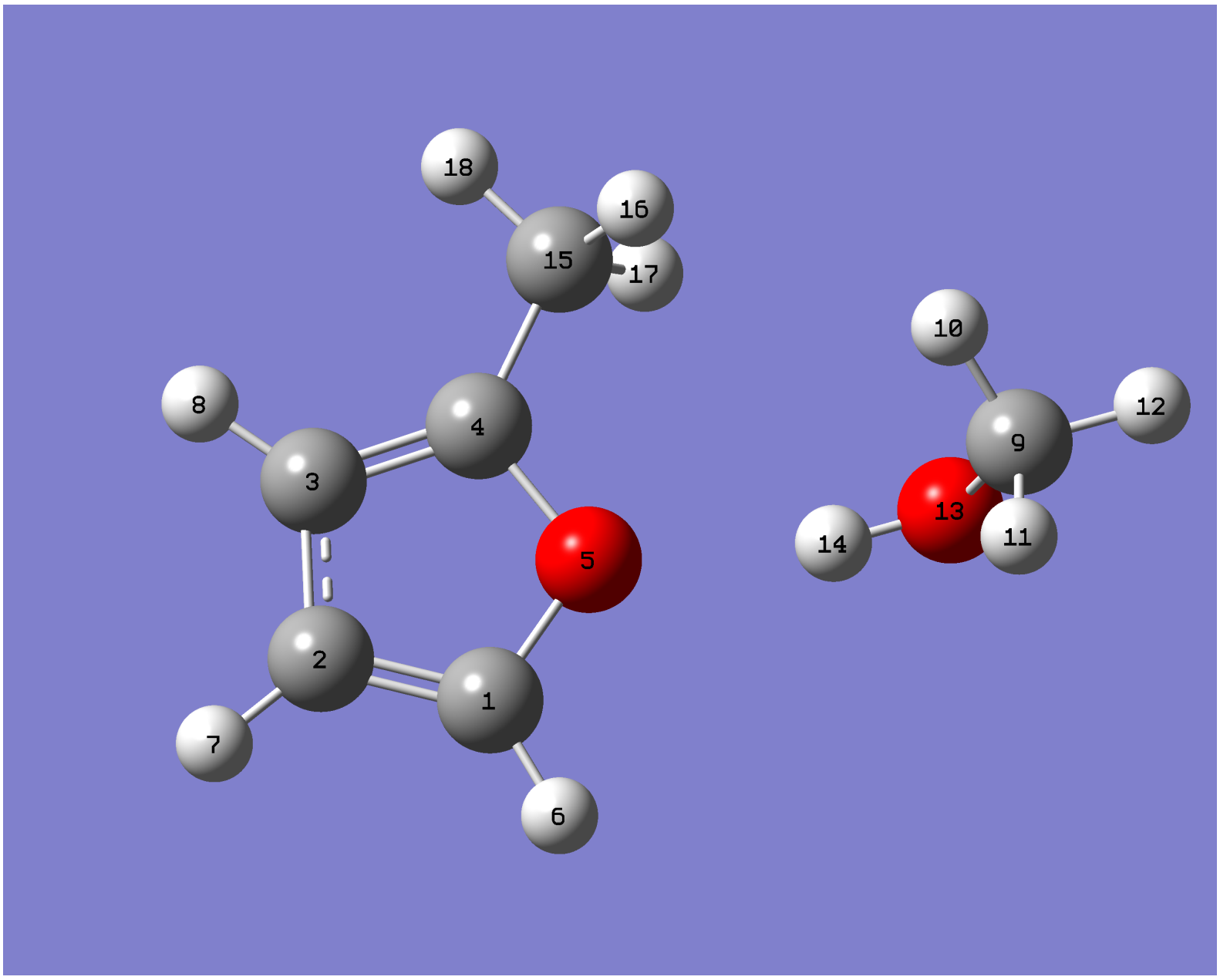

Figure S11: OH-bonded methanol – 2-methylfuran structure in planar conformation Op.

Table S11: Methanol – 2-methylfuran Op

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-1.2239690	-1.4530480	0.0135200
2	C	1			1.3577340			-2.4665860	-0.9089770	0.0712380
3	C	2	1		1.4373426	106.3034226		-2.2836460	0.5166520	0.0629570
4	C	3	2	1	1.3621036	106.9802515	0.0099203	-0.9423090	0.7452260	0.0005450
5	O	1	2	3	1.3716503	109.9633127	0.0378043	-0.2792560	-0.4595150	-0.0293070
6	H	1	2	3	1.0760363	134.1783084	-179.7003652	-0.8467590	-2.4605680	-0.0081620
7	H	2	1	5	1.0778355	126.1973040	179.9817245	-3.3973680	-1.4508160	0.1134830
8	H	3	2	1	1.0780416	127.2730505	179.9622150	-3.0505310	1.2735060	0.0980720
9	C	5	1	2	3.5042250	135.5161795	162.5769665	3.1716290	-0.2643980	0.5476810
10	H	9	5	1	1.0966420	77.2799972	-132.3813830	2.7831350	0.5892130	1.1160510
11	H	9	5	1	1.0959115	85.4295841	-22.1602938	3.0344660	-1.1729760	1.1449200
12	H	9	5	1	1.0896693	161.6171016	117.6334093	4.2393770	-0.1137280	0.3908630
13	O	9	5	1	1.4188012	55.2466482	98.8802029	2.5704940	-0.3705560	-0.7330860
14	H	13	9	5	0.9633401	107.5497355	-6.4513465	1.6265450	-0.5096630	-0.6002940
15	C	4	3	2	1.4859542	134.2529128	-179.7789498	-0.0993920	1.9684720	-0.0343860
16	H	15	4	3	1.0933461	111.1772958	116.2975342	0.5391230	2.0335620	0.8507510
17	H	15	4	3	1.0924948	111.2281153	-123.5198317	0.5473380	1.9782070	-0.9148350
18	H	15	4	3	1.0900169	109.4732252	-3.3639008	-0.7395890	2.8502740	-0.0610290

S1.2.4 2-methylfuran OH transition state OmedTS

up to table of contents

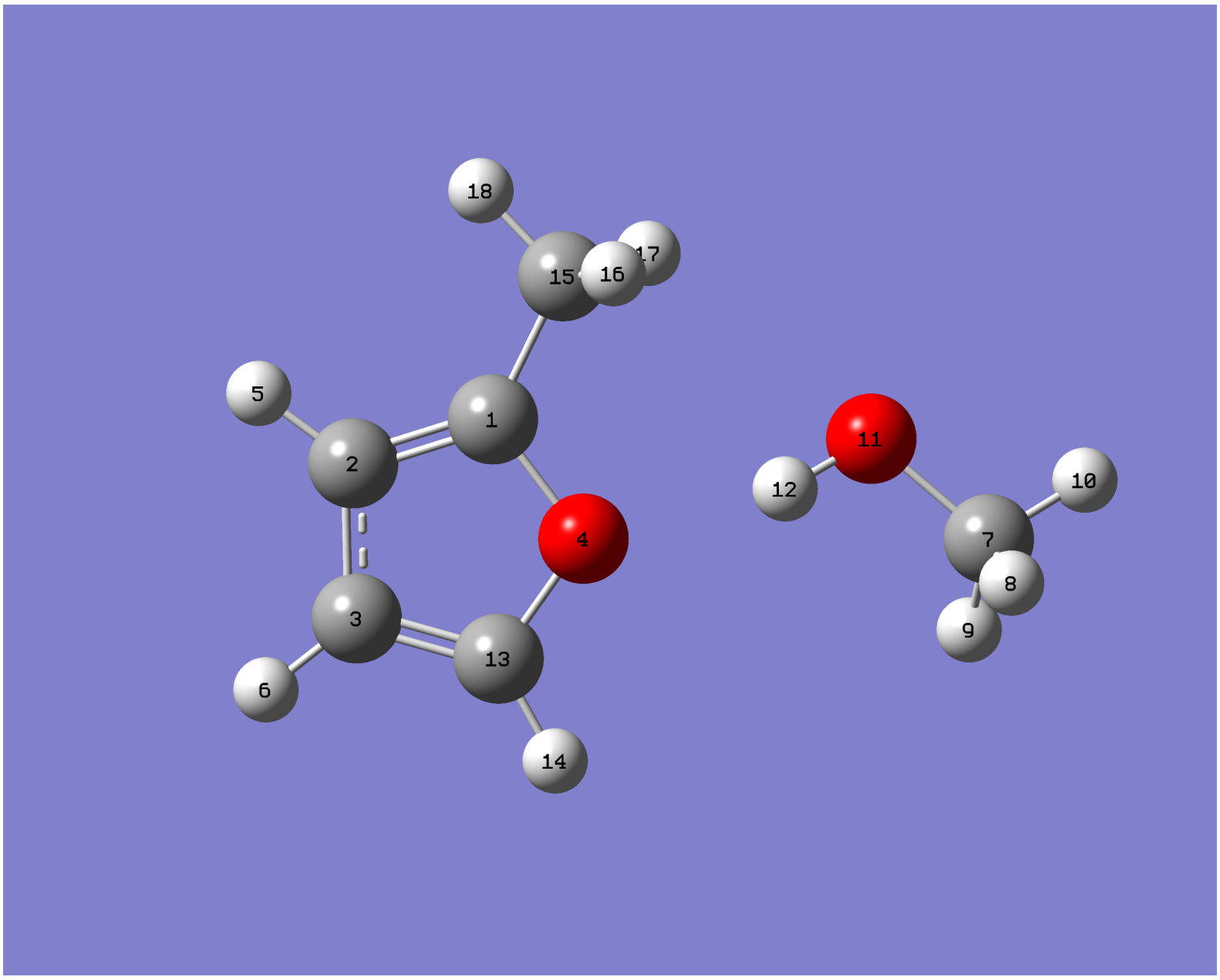

Figure S12: OH-bonded methanol – 2-methylfuran transition state with medium energy.

Table S12: OH-bonded methanol – 2-methylfuran transition state with medium energy.

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-1.0885510	0.7142490	0.0543410
2	C	1			1.3621965			-2.3414910	0.2879950	-0.2681930
3	C	2	1		1.4372184	107.0269490		-2.3330980	-1.1466270	-0.1822510
4	O	1	2	3	1.3764705	109.1553546	-0.0385178	-0.2991470	-0.3771750	0.3377240
5	H	2	1	4	1.0780317	125.7053390	179.9252621	-3.1722630	0.9211330	-0.5348510
6	H	3	2	1	1.0779008	127.5144546	179.9519607	-3.1534510	-1.8202430	-0.3696880
7	C	4	1	2	3.8267156	126.4161011	153.7791051	3.5064800	-0.5795940	-0.0086600
8	H	7	4	1	1.0961018	88.3713507	120.0324070	3.5614370	-0.7943390	1.0647940
9	H	7	4	1	1.0961879	89.3262995	-131.1379780	3.3937430	-1.5245760	-0.5526520
10	H	7	4	1	1.0895460	149.2785314	-4.6249901	4.4449820	-0.1184470	-0.3147120
11	O	7	4	1	1.4190850	42.1120734	-6.2123517	2.4688150	0.3384730	-0.3155910
12	H	11	7	4	0.9634177	108.3743552	-0.7696611	1.6291870	-0.0523820	-0.0502030
13	C	3	2	1	1.3576896	106.2823144	-0.0250909	-1.0747330	-1.4985170	0.1865470
14	H	13	3	2	1.0760564	134.0802060	179.9815322	-0.5855510	-2.4378490	0.3769510
15	C	1	2	3	1.4861223	134.2405529	-179.8525982	-0.4420190	2.0482910	0.1586860
16	H	15	1	2	1.0931466	111.0927092	116.6031404	-0.1205740	2.2505760	1.1837340
17	H	15	1	2	1.0923308	111.2262775	-123.4586400	0.4389170	2.1121880	-0.4840080
18	H	15	1	2	1.0901047	109.3550555	-3.1329697	-1.1532980	2.8187790	-0.1392380

S1.2.5 2-methylfuran OH transition state OhiTS

up to table of contents

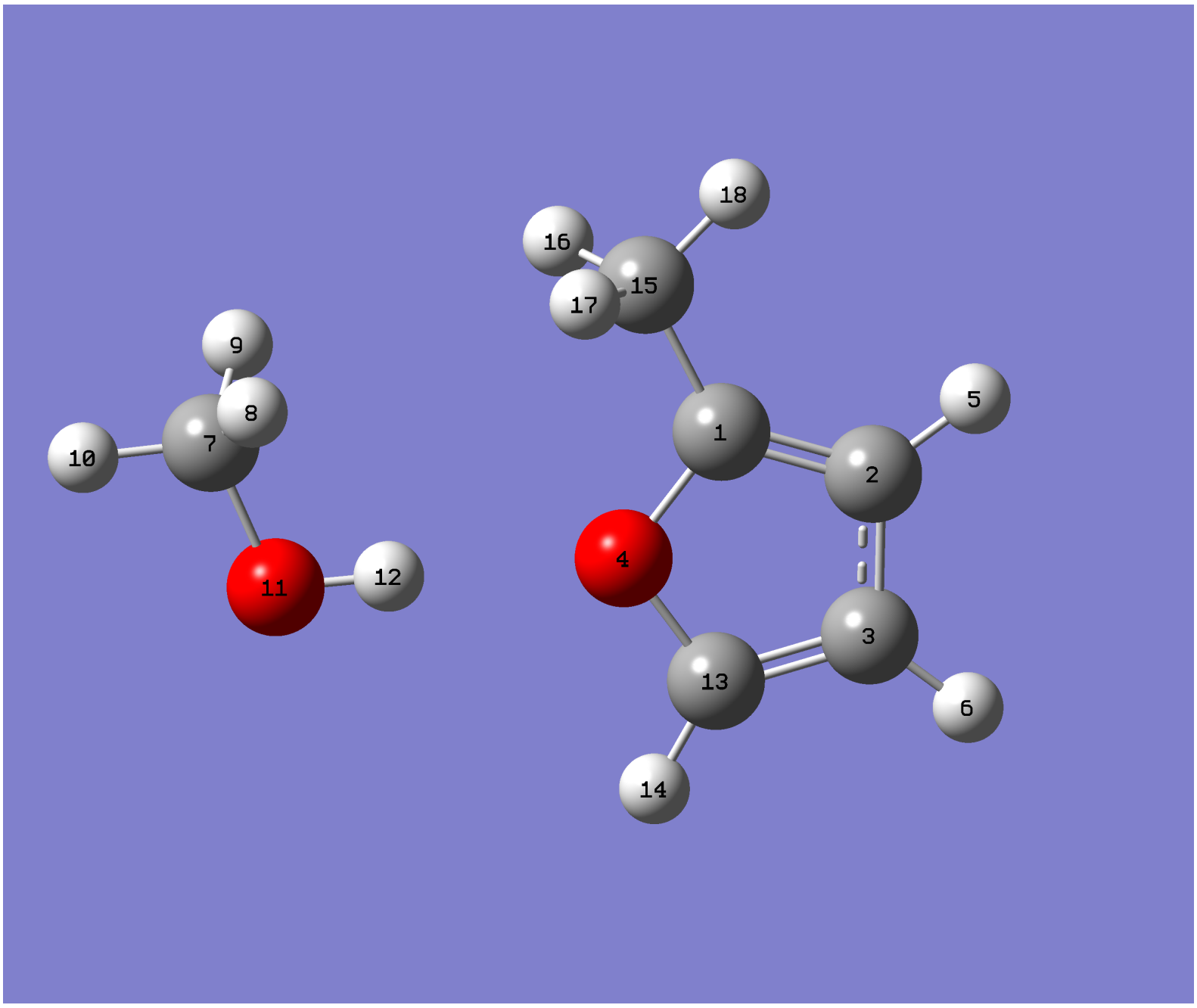

Figure S13: OH-bonded methanol – 2-methylfuran transition state with highest energy.

Table S13: OH-bonded methanol – 2-methylfuran transition state with highest energy.

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							0.9878730	0.7636710	0.0079990
2	C	1			1.3620972			2.3242900	0.5088470	-0.0580540
3	C	2	1		1.4373158	106.9295314		2.4794890	-0.9199080	-0.0368590
4	O	1	2	3	1.3742104	109.2545820	0.0492780	0.3022910	-0.4256810	0.0702360
5	H	2	1	4	1.0780718	125.7788935	-179.9499792	3.1051960	1.2499150	-0.1150000
6	H	3	2	1	1.0777845	127.4988071	-179.9785036	3.3992070	-1.4805820	-0.0740460
7	C	4	1	2	3.6623147	110.1800165	-175.4536211	-3.3066970	0.1900350	-0.0227620
8	H	7	4	1	1.0966319	82.9564800	-58.1821012	-3.0911670	0.7884340	0.8705840
9	H	7	4	1	1.0967865	85.7602440	51.2783317	-3.0978710	0.7974790	-0.9117750
10	H	7	4	1	1.0896585	157.1630160	-179.5104681	-4.3679850	-0.0569820	-0.0203050
11	O	7	4	1	1.4175041	50.0150577	175.0372995	-2.5908850	-1.0334280	-0.0310940
12	H	11	7	4	0.9633810	107.9357180	-0.9111330	-1.6500960	-0.8268520	-0.0125120
13	C	3	2	1	1.3577830	106.3035766	-0.0378298	1.2269900	-1.4382480	0.0415290
14	H	13	3	2	1.0761266	134.2660570	179.9381523	0.8286780	-2.4370900	0.0828900
15	C	1	2	3	1.4857427	134.1603796	179.8415972	0.1704860	2.0041830	0.0289730
16	H	15	1	2	1.0931429	111.2478116	120.1608980	-0.5205450	2.0376370	-0.8173830
17	H	15	1	2	1.0931620	111.2500243	-119.3629722	-0.4169850	2.0760800	0.9480550
18	H	15	1	2	1.0900012	109.5310514	0.4111109	0.8257280	2.8733470	-0.0285990

S1.2.6 2-methylfuran transition state between OH- and π-bonded conformation

up to table of contents

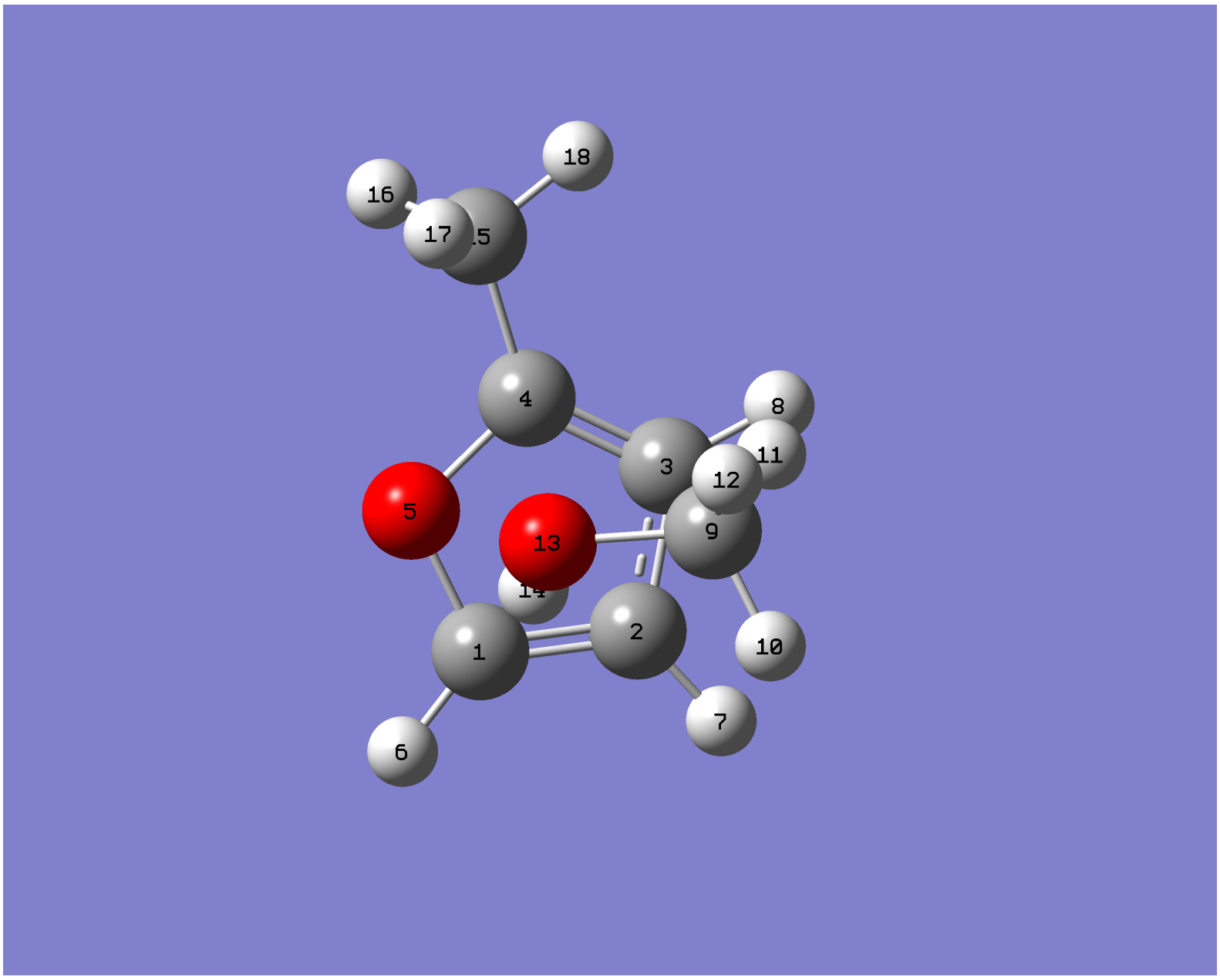

Figure S14: Methanol – 2-methylfuran transition state between OH- and π-bonded conformation.

Table S14: Methanol – 2-methylfuran transition state between OH- and π-bonded conformation.

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							1.1023710	-1.3838780	-0.6839190
2	C	1			1.3615959			0.8987720	-1.5494550	0.6521480
3	C	2	1		1.4363549	106.1328167		0.8289490	-0.2285220	1.2119480
4	C	3	2	1	1.3647120	106.7484894	0.2490999	0.9892560	0.6462640	0.1768200
5	O	1	2	3	1.3680936	110.1054161	-0.1315719	1.1603300	-0.0515490	-0.9892390
6	H	1	2	3	1.0763249	133.9643932	178.4153909	1.2409740	-2.0618680	-1.5082940
7	H	2	1	5	1.0781456	126.2427264	-179.5494357	0.8185880	-2.4900590	1.1729480
8	H	3	2	1	1.0781060	127.3569796	-179.9286262	0.6768610	0.0366290	2.2458130
9	C	3	2	1	3.6743201	90.3754275	85.6894605	-2.7556730	-0.0576160	0.4233390
10	H	9	3	2	1.0955522	99.8640878	36.0986534	-3.0390030	-1.0991160	0.6110530
11	H	9	3	2	1.0951479	45.5268357	142.8050700	-2.1352650	0.2944470	1.2542990
12	H	9	3	2	1.0895709	147.7541864	-172.4080454	-3.6624760	0.5450300	0.3822180
13	O	9	3	2	1.4209169	75.1554467	-74.2407074	-2.0998960	0.0989030	-0.8274460
14	H	13	9	3	0.9613732	107.8486179	34.4956302	-1.3042430	-0.4404970	-0.8125340
15	C	4	3	2	1.4847179	133.8924524	176.4655235	0.9529500	2.1263100	0.0648690
16	H	15	4	3	1.0924948	111.1649716	127.1621556	1.8555140	2.5075910	-0.4183990
17	H	15	4	3	1.0930375	110.3964062	-112.5873654	0.0880000	2.4427090	-0.5237600
18	H	15	4	3	1.0902117	109.6647084	7.0575198	0.8778210	2.5676870	1.0589030

S1.2.7 2-methylfuran π-bonded conformation of lowest energy PI

up to table of contents

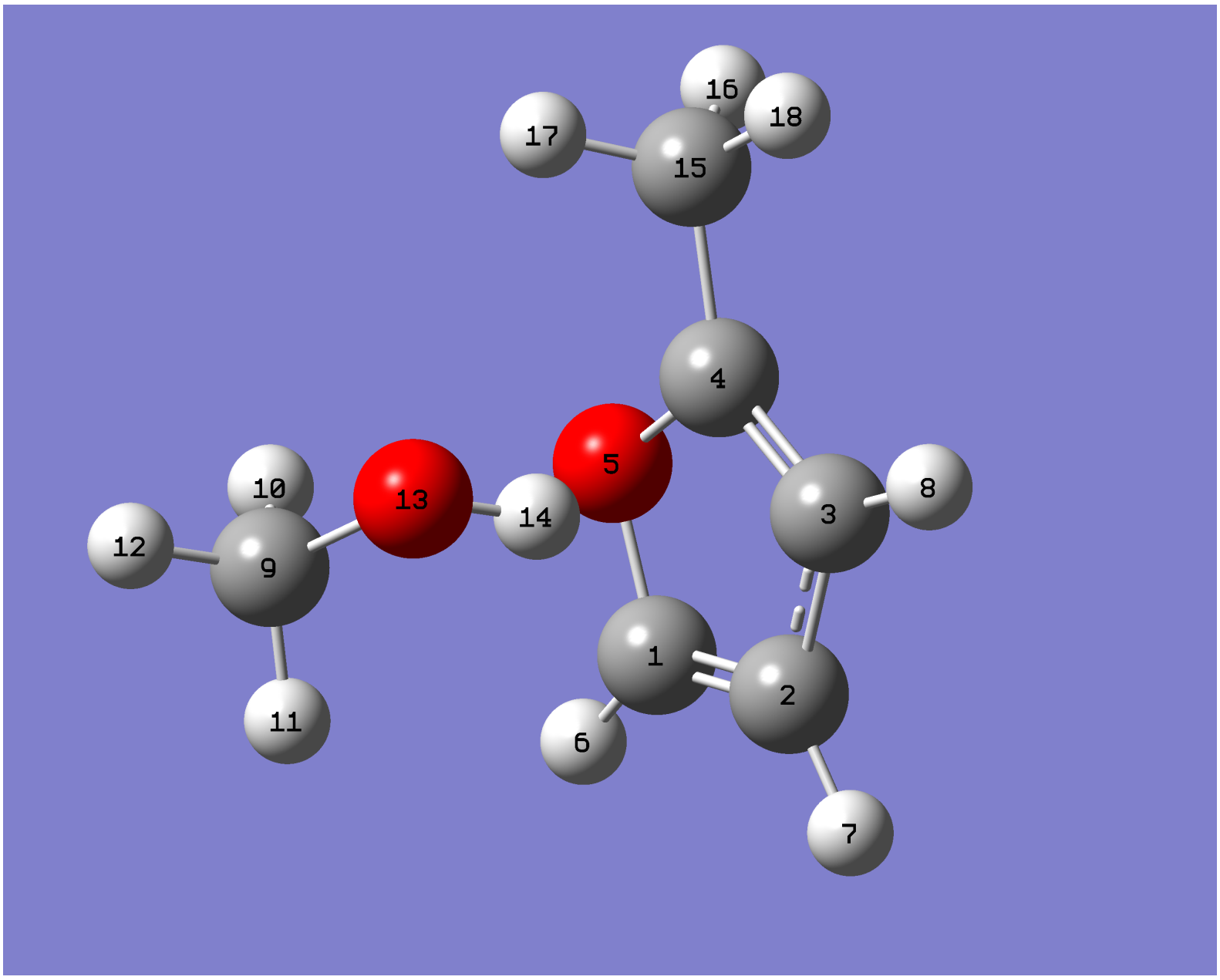

Figure S15: π-bonded methanol – 2-methylfuran structure in lowest-energy conformation.

Table S15: π-bonded methanol – 2-methylfuran structure, lowest-energy conformation.

#	N	ref atom A	B	C	Bond	Angle	Dihedral	X	Y	Z
1	C							0.9528780	-1.4355590	-0.6690640
2	C	1			1.3598263			1.0836070	-1.4847390	0.6835700
3	C	2	1		1.4377321	106.0481361		1.0887010	-0.1188390	1.1323070
4	C	3	2	1	1.3665082	106.7308721	0.0186028	0.9600940	0.6617640	0.0180970
5	O	1	2	3	1.3672145	110.2572723	-0.1451021	0.8733950	-0.1372100	-1.0900720
6	H	1	2	3	1.0761601	133.8800448	179.8761818	0.9014250	-2.1834190	-1.4411900
7	H	2	1	5	1.0778855	126.4014389	-179.8466875	1.1703910	-2.3744070	1.2858960
8	H	3	2	1	1.0785502	127.4202959	-179.1210992	1.1889030	0.2378730	2.1452170
9	C	5	1	2	3.4965703	87.1923567	-85.8597534	-2.5621170	-0.3260000	-0.4674810
10	H	9	5	1	1.0951562	44.2926193	-130.9017264	-1.9334220	0.0100040	-1.2988720
11	H	9	5	1	1.0953960	89.2198971	-12.6816391	-2.4704820	-1.4136660	-0.3754050
12	H	9	5	1	1.0895905	152.4704100	-144.2746725	-3.5998480	-0.0826540	-0.6935440
13	O	9	5	1	1.4221955	84.3284611	99.4079125	-2.2355100	0.3383280	0.7468650
14	H	13	9	5	0.9627973	107.6876335	-25.4696020	-1.3182970	0.1327190	0.9552490
15	C	4	3	2	1.4855313	133.8107959	178.8609098	0.8763890	2.1278480	-0.2063900
16	H	15	4	3	1.0926415	111.0219422	123.1967405	1.6612720	2.4655400	-0.8874100
17	H	15	4	3	1.0927524	110.9103550	-116.3153328	-0.0910110	2.4023120	-0.6340750
18	H	15	4	3	1.0899568	109.5777821	3.1725157	0.9906870	2.6499040	0.7435570

S1.2.8 2-methylfuran π-bonded low TS PiloTS

up to table of contents

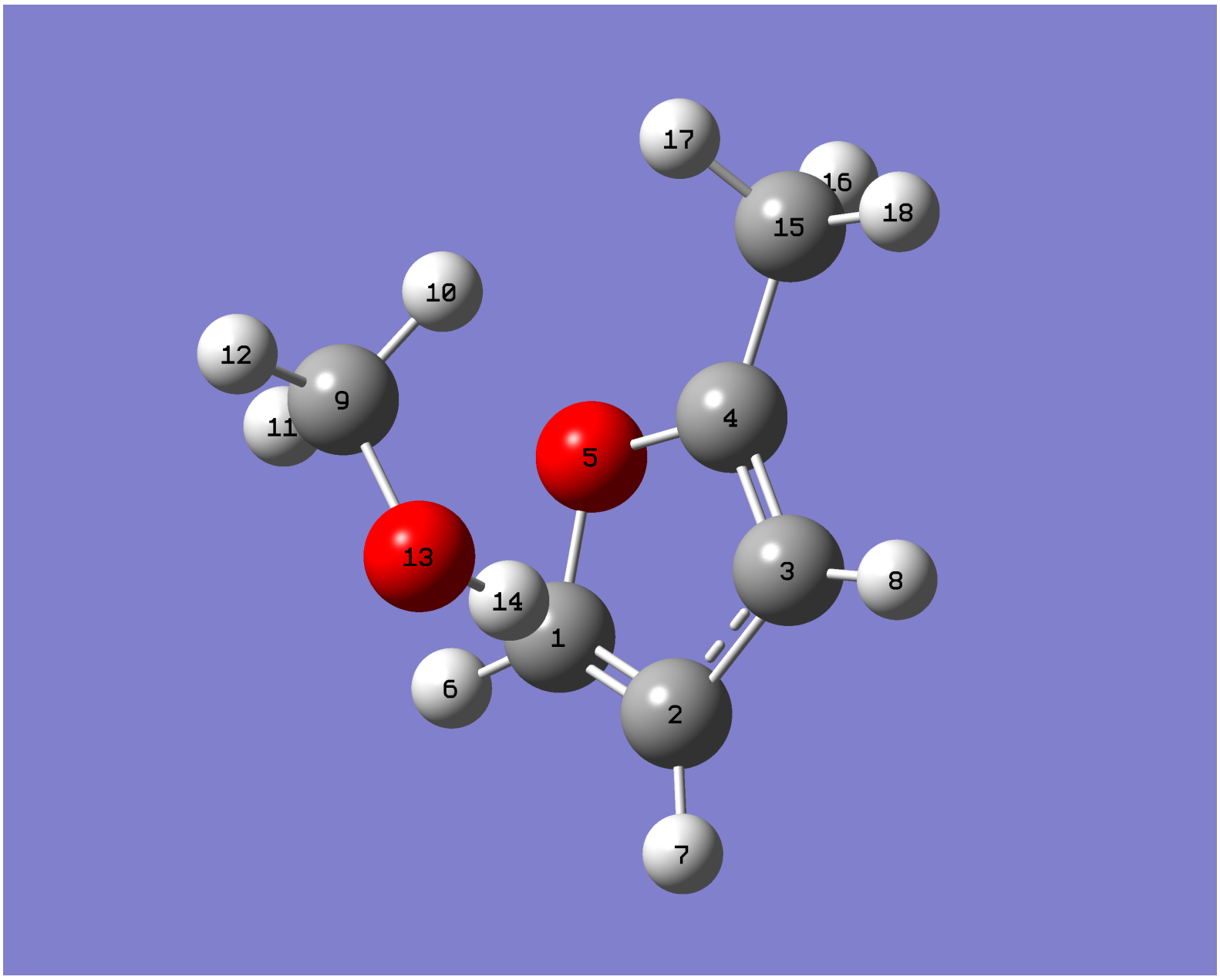

Figure S16: π-bonded methanol – 2-methylfuran transition state of lowest energy.

Table S16: π-bonded methanol – 2-methylfuran transition state of lowest energy.

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							0.5944270	-1.4140800	-0.8804240
2	C	1			1.3612674			0.5356910	-1.6907560	0.4511350
3	C	2	1		1.4380496	106.0370984		0.8964850	-0.4733140	1.1261530
4	C	3	2	1	1.3651899	106.6883387	-0.1058939	1.1501820	0.4526860	0.1556350
5	O	1	2	3	1.3657140	110.2279048	0.0900834	0.9671630	-0.1149710	-1.0767870
6	H	1	2	3	1.0761709	133.8093541	-179.9443435	0.4134790	-1.9919250	-1.7700850
7	H	2	1	5	1.0781926	126.3185877	-179.4476908	0.2773200	-2.6384620	0.8956540
8	H	3	2	1	1.0782216	127.3866979	-179.7701254	0.9637980	-0.3096630	2.1897550
9	C	5	1	2	3.5246085	88.2113605	-80.8591939	-2.3730320	0.8219120	-0.4537200
10	H	9	5	1	1.0959496	69.8743231	152.5834567	-1.6954430	1.6403080	-0.1850070
11	H	9	5	1	1.0953489	55.4911004	-75.6626782	-2.0199260	0.3653870	-1.3846820
12	H	9	5	1	1.0895795	159.5633537	-118.3536312	-3.3657520	1.2372770	-0.6244900
13	O	9	5	1	1.4200027	91.9399045	39.9581946	-2.4952420	-0.1293630	0.5934420
14	H	13	9	5	0.9621777	107.4117479	5.0460338	-1.6301020	-0.5309900	0.7199900
15	C	4	3	2	1.4857215	133.8041875	-179.5634065	1.5702500	1.8776050	0.1783750
16	H	15	4	3	1.0929817	111.0921536	117.7761618	2.5403070	2.0095010	-0.3076310
17	H	15	4	3	1.0927851	111.1326212	-122.0551713	0.8456830	2.5102750	-0.3401910
18	H	15	4	3	1.0900375	109.6075709	-2.1216443	1.6512550	2.2186520	1.2105120

S1.2.9 2-methylfuran π-bonded conformation of high energy PIb

up to table of contents

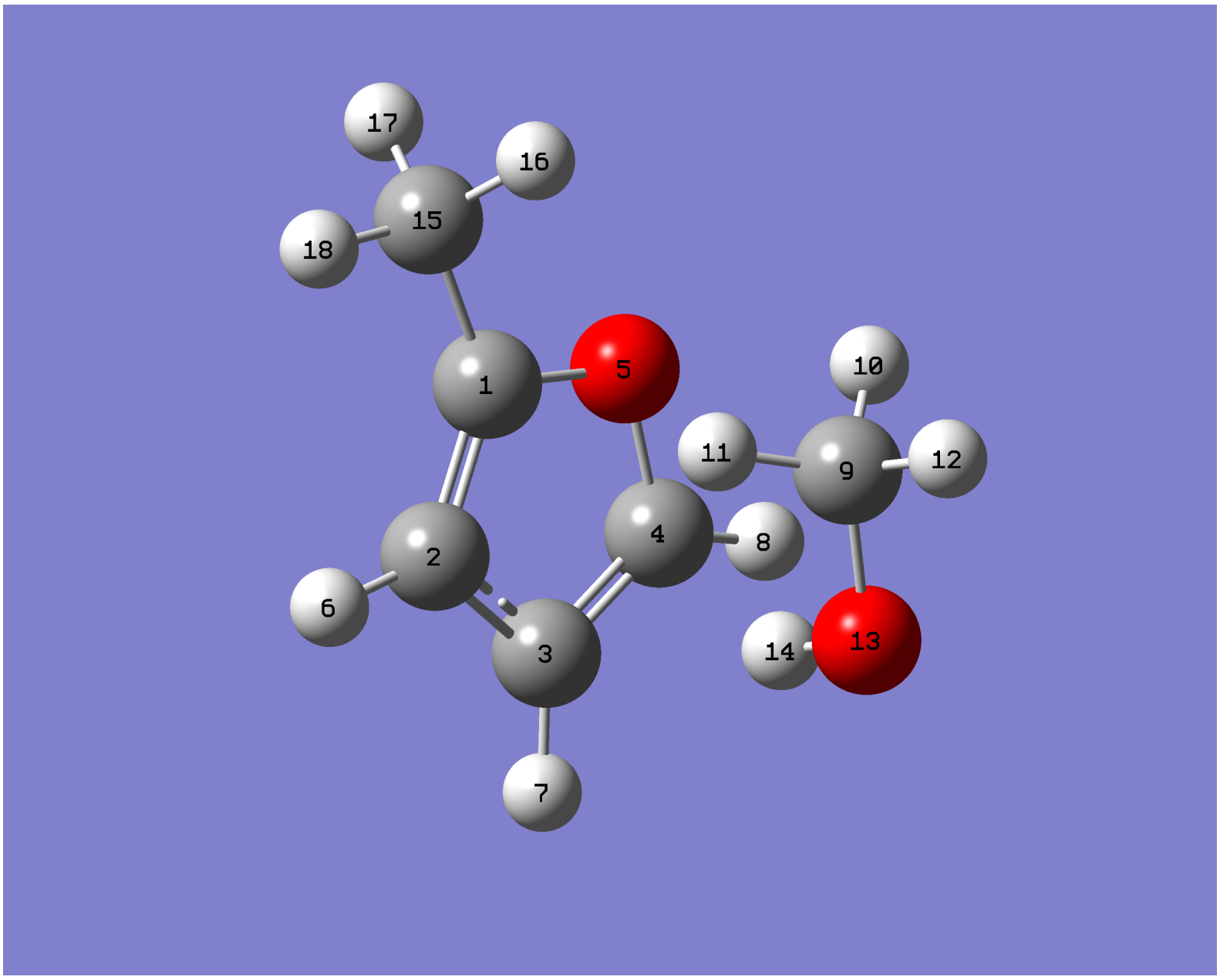

Figure S17: π-bonded methanol – 2-methylfuran structure in high-energy conformation.

Table S17: π-bonded methanol – 2-methylfuran structure, high-energy conformation.

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-1.1684050	0.4365480	0.1175140
2	C	1			1.3642477			-0.9747610	-0.4572280	1.1298570
3	C	2	1		1.4374330	106.7018956		-0.5444560	-1.6855790	0.5197710
4	C	3	2	1	1.3619236	106.0744256	0.1039445	-0.5056980	-1.4475480	-0.8206300
5	O	4	3	2	1.3659647	110.1771542	0.0288272	-0.8805940	-0.1602190	-1.0815830
6	H	2	1	5	1.0780611	125.9862463	179.8697893	-1.1213290	-0.2657490	2.1806040
7	H	3	2	1	1.0782644	127.6041685	-179.2779120	-0.3078840	-2.6162500	1.0102190
8	H	4	3	2	1.0762508	133.8587833	-179.9470552	-0.2497610	-2.0466430	-1.6773080
9	C	1	2	3	3.5199455	91.1717794	-79.3279000	2.2908720	1.0499550	-0.0996280
10	H	9	1	2	1.0955701	64.9576056	149.2854322	1.7418970	1.1510440	-1.0423270
11	H	9	1	2	1.0959090	61.9279601	-80.0060589	1.7265670	1.5536860	0.6933610
12	H	9	1	2	1.0896594	162.9190106	-139.5021915	3.2565870	1.5435160	-0.2052200
13	O	9	1	2	1.4202944	90.0217350	34.9587178	2.5524210	-0.3092940	0.2186020
14	H	13	9	1	0.9625402	107.8193579	3.3157171	1.7066060	-0.7632160	0.2895630
15	C	1	2	3	1.4854832	133.8707342	-179.6669352	-1.5976890	1.8577540	0.0670260
16	H	15	1	2	1.0930555	111.0711875	119.5291136	-0.8240040	2.4862750	-0.3814640
17	H	15	1	2	1.0928205	111.1034225	-120.3034492	-2.5094220	1.9726170	-0.5244180
18	H	15	1	2	1.0901012	109.6306032	-0.3774839	-1.7930570	2.2174220	1.0773680

S1.2.10 2-methylfuran π-bonded high TS PihiTS

up to table of contents

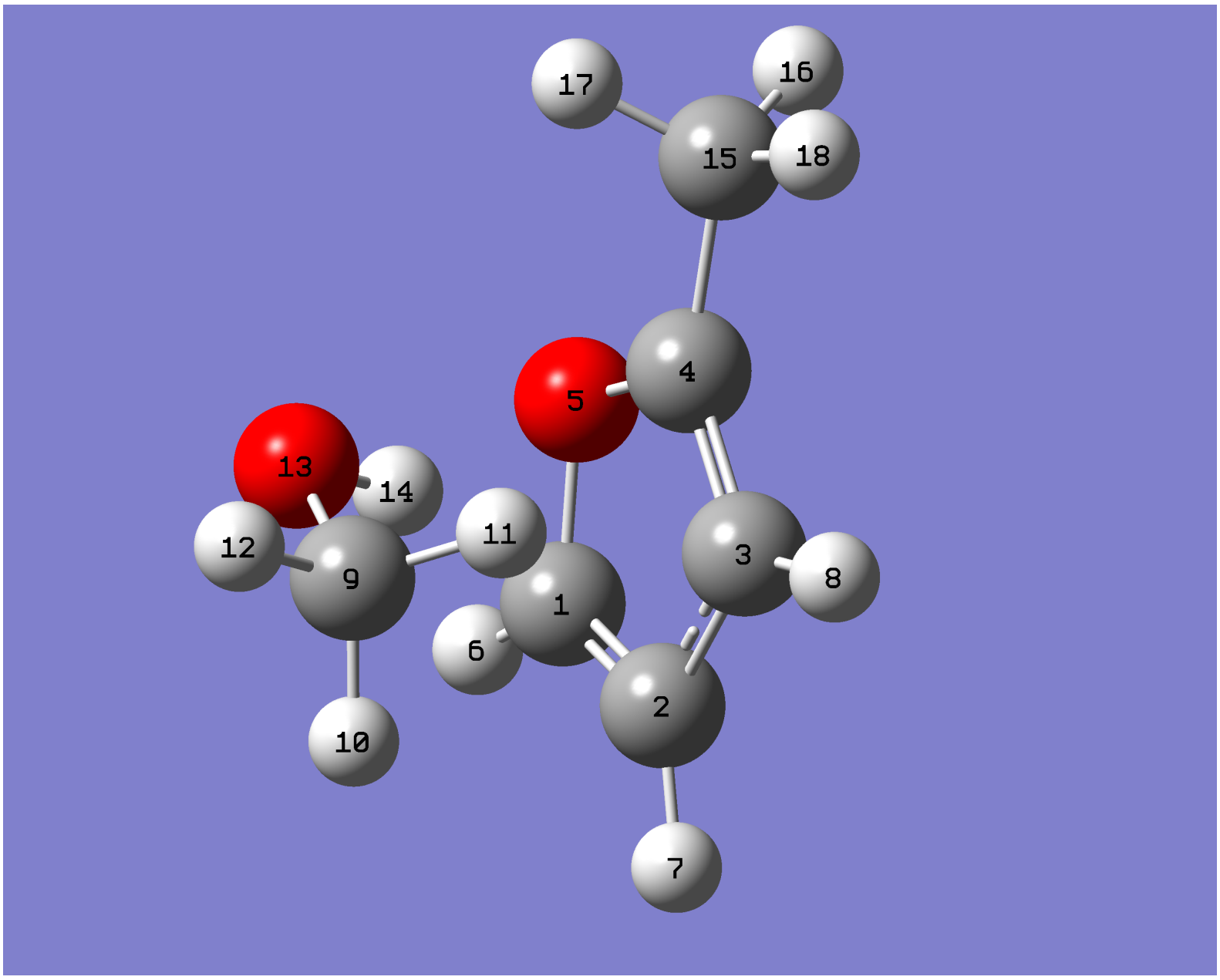

Figure S18: π-bonded methanol – 2-methylfuran transition state of highest energy.

Table S18: π-bonded methanol – 2-methylfuran transition state of highest energy.

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							1.4819020	-1.3347940	-0.5904200
2	C	1			1.3602065			0.8773970	-1.5607790	0.6069380
3	C	2	1		1.4376219	106.0180655		0.5533160	-0.2649670	1.1385390
4	C	3	2	1	1.3663549	106.7479863	-0.0018359	0.9848860	0.6546570	0.2247750
5	O	1	2	3	1.3665041	110.2609799	-0.0681769	1.5537520	0.0070880	-0.8384600
6	H	1	2	3	1.0760621	133.8780997	-179.6860720	1.8925440	-1.9753860	-1.3512910
7	H	2	1	5	1.0778812	126.3724137	-179.8940866	0.6884780	-2.5221530	1.0562680
8	H	3	2	1	1.0784392	127.4277597	-179.3701463	0.0734000	-0.0434740	2.0785670
9	C	3	2	1	3.7373187	98.4640771	99.9519140	-3.0630720	-0.1740590	0.1999100
10	H	9	3	2	1.0958190	84.9071428	37.8965419	-3.0562040	-1.2391220	0.4576170
11	H	9	3	2	1.0963057	67.6069306	150.6072605	-2.8514330	0.4089480	1.1039000
12	H	9	3	2	1.0894976	166.4775975	-133.9893650	-4.0593230	0.0890980	-0.1539790
13	O	9	3	2	1.4196327	64.7294269	-79.3909316	-2.1565470	0.1253700	-0.8507620
14	H	13	9	3	0.9625112	107.2906970	10.1588257	-1.2723220	-0.0858090	-0.5345700
15	C	4	3	2	1.4856483	133.8103311	178.9706351	0.9383730	2.1380680	0.1578490
16	H	15	4	3	1.0926855	111.0430079	122.2544245	1.9424650	2.5581420	0.0614190
17	H	15	4	3	1.0927549	110.8789406	-117.3621250	0.3447020	2.4709220	-0.6970640
18	H	15	4	3	1.0900969	109.5648058	2.2948826	0.4832300	2.5304250	1.0673610

S1.3 Methanol – 2,5-dimethylfuran system

S1.3.1 2,5-dimethylfuran OH top Ot

up to table of contents

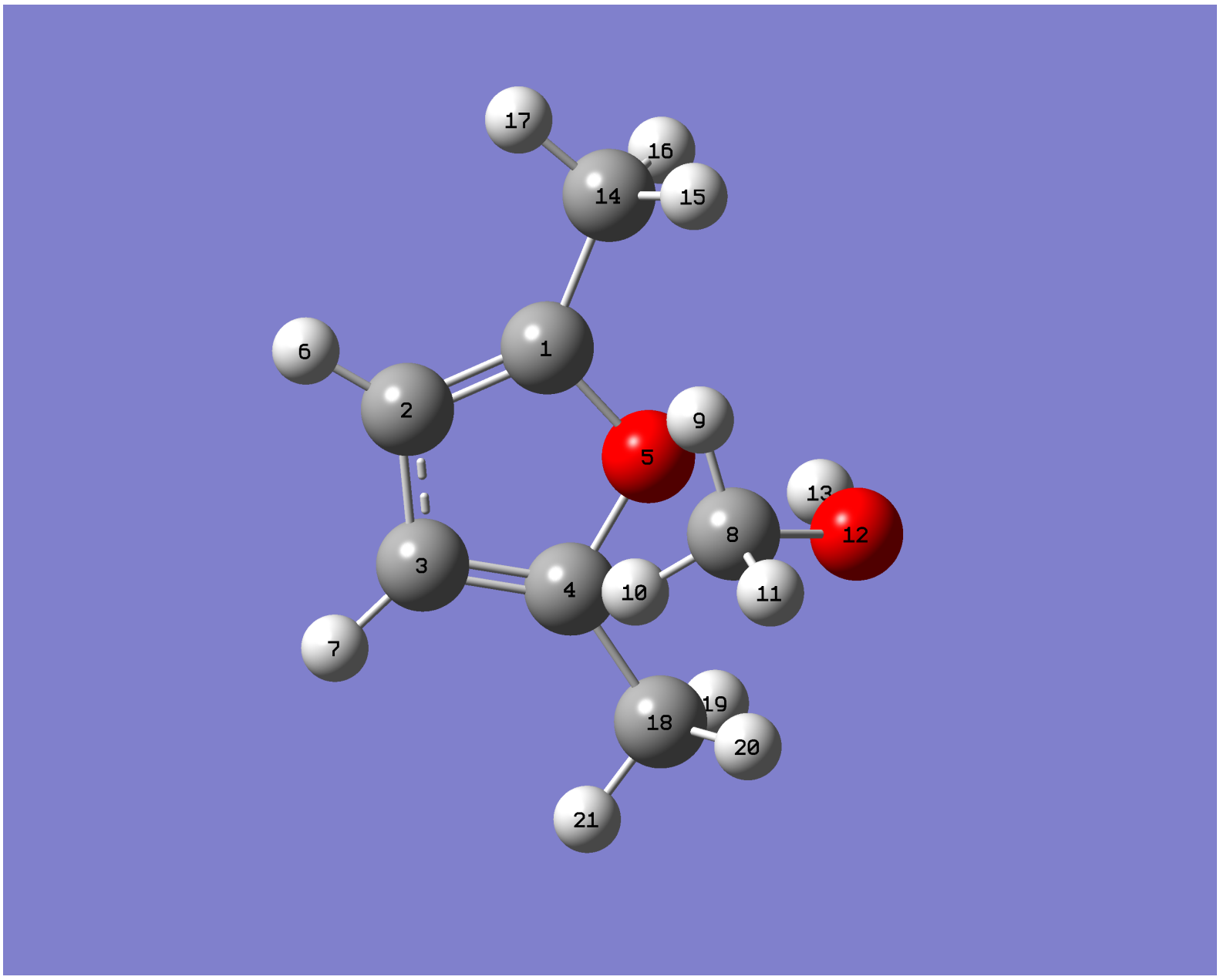

Figure S19: OH-bonded methanol – 2,5-dimethylfuran structure in top conformation Ot.

Table S19: OH-bonded methanol – 2,5-dimethylfuran top conformation Ot

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-1.1060320	0.8807050	-0.1443340
2	C	1			1.3606396			-1.7797440	0.2992760	0.8849340
3	C	2	1		1.4383124	106.8589974		-1.4001020	-1.0879330	0.9012340
4	C	3	2	1	1.3608960	106.9146967	-0.0103810	-0.5179840	-1.2690460	-0.1191110
5	O	1	2	3	1.3777171	109.1845517	0.0803895	-0.3291250	-0.0690550	-0.7708130
6	H	2	1	5	1.0783536	125.7759046	-179.8413457	-2.4653680	0.7980210	1.5512820
7	H	3	2	1	1.0783591	127.3534767	-179.9129006	-1.7404540	-1.8514500	1.5824540
8	C	5	1	2	3.2434251	92.1830933	-93.9863703	2.2648730	0.6912930	1.0216300
9	H	8	5	1	1.0961751	89.1422284	-25.6445076	1.8545230	1.6985020	1.1585340
10	H	8	5	1	1.0954770	63.7772661	85.5886399	1.5683590	-0.0315260	1.4603450
11	H	8	5	1	1.0896237	162.4522977	153.8086921	3.2133260	0.6308510	1.5546060
12	O	8	5	1	1.4218537	64.7881754	-140.5515004	2.5351940	0.4075170	-0.3451420
13	H	12	8	5	0.9627219	107.0458543	10.1108665	1.6861850	0.3576190	-0.7962820
14	C	1	2	3	1.4856127	134.3661679	-179.9342226	-1.0430260	2.2576460	-0.6985080
15	H	14	1	2	1.0937604	111.3658938	120.0634945	-0.0258460	2.6575990	-0.6573460
16	H	14	1	2	1.0931568	111.2264307	-119.5934785	-1.3700130	2.2799060	-1.7413770
17	H	14	1	2	1.0902243	109.5234253	0.2600477	-1.6931030	2.9136580	-0.1191660
18	C	4	3	2	1.4857789	134.4461718	179.4536493	0.2475990	-2.4316430	-0.6385240
19	H	18	4	3	1.0932694	111.1678085	119.4680209	-0.0186700	-2.6477150	-1.6766240
20	H	18	4	3	1.0932559	111.0254741	-120.2319847	1.3236230	-2.2427310	-0.5973760
21	H	18	4	3	1.0902501	109.4853772	-0.3038127	0.0253880	-3.3122250	-0.0353300

S1.3.2 2,5-dimethylfuran OH planar Op

up to table of contents

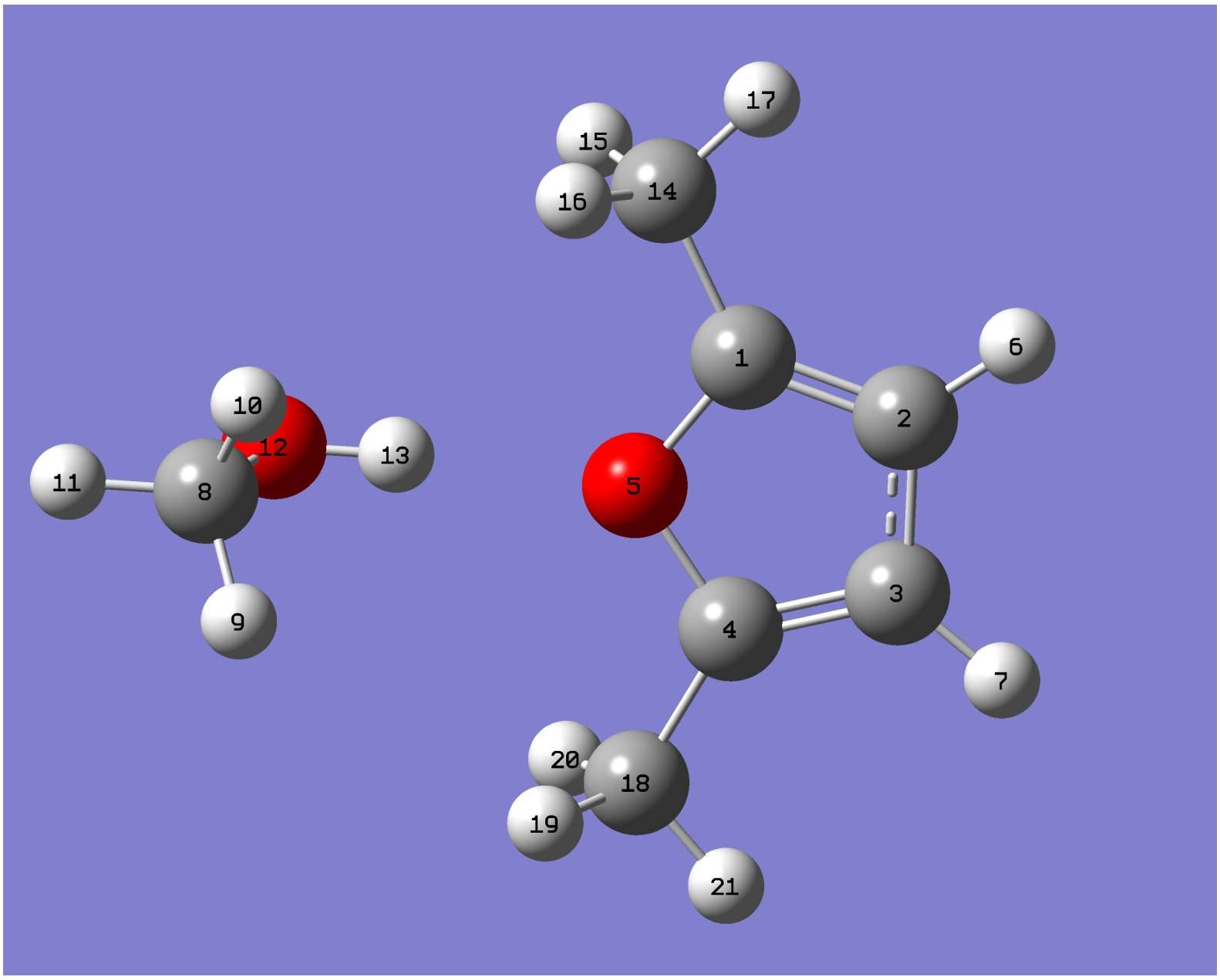

Figure S20: OH-bonded methanol – 2,5-dimethylfuran structure in planar conformation Op.

Table S20: OH-bonded methanol – 2,5-dimethylfuran planar conformation Op

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							0.9984110	1.1153250	-0.0038870
2	C	1			1.3603022			2.2929990	0.7193940	0.1291640
3	C	2	1		1.4387920	106.9214119		2.2929970	-0.7193980	0.1291640
4	C	3	2	1	1.3603023	106.9214372	0.0000000	0.9984080	-1.1153260	-0.0038870
5	O	4	3	2	1.3777897	109.0311424	-0.0368402	0.1936410	0.0000000	-0.0857550
6	H	2	1	5	1.0782661	125.7497556	-179.9949281	3.1459600	1.3732410	0.2163390
7	H	3	2	1	1.0782664	127.3288563	179.9675782	3.1459560	-1.3732480	0.2163390
8	C	5	4	3	3.4367874	124.0643833	-158.7293086	-3.1725650	0.0000010	0.6071840
9	H	8	5	4	1.0964714	80.3412822	22.3071638	-2.8687120	-0.8900590	1.1708470
10	H	8	5	4	1.0964710	80.3412763	133.1646154	-2.8687110	0.8900590	1.1708490
11	H	8	5	4	1.0897773	164.0914697	-102.2641681	-4.2593080	0.0000020	0.5259180
12	O	8	5	4	1.4184540	56.8278094	-102.2641422	-2.6517730	0.0000030	-0.7122050
13	H	12	8	5	0.9638004	107.2280552	0.0000000	-1.6907010	0.0000020	-0.6397360
14	C	1	2	3	1.4857159	134.5255233	179.9528253	0.3135100	2.4319230	-0.0734010
15	H	14	1	2	1.0930601	111.2927416	121.2130830	-0.2454340	2.5398020	-1.0065270
16	H	14	1	2	1.0934732	111.2685088	-118.5039617	-0.3897490	2.5573890	0.7544690
17	H	14	1	2	1.0901695	109.4995425	1.2572694	1.0536830	3.2304680	-0.0191860
18	C	4	3	2	1.4857164	134.5255101	-179.9528287	0.3135040	-2.4319230	-0.0734010
19	H	18	4	3	1.0934722	111.2684996	118.5039944	-0.3897550	-2.5573870	0.7544680
20	H	18	4	3	1.0930603	111.2926655	-121.2131585	-0.2454410	-2.5397990	-1.0065270
21	H	18	4	3	1.0901688	109.4995384	-1.2573240	1.0536750	-3.2304690	-0.0191870

S1.3.3 2,5-dimethylfuran OH high-energy TS OhiTS

up to table of contents

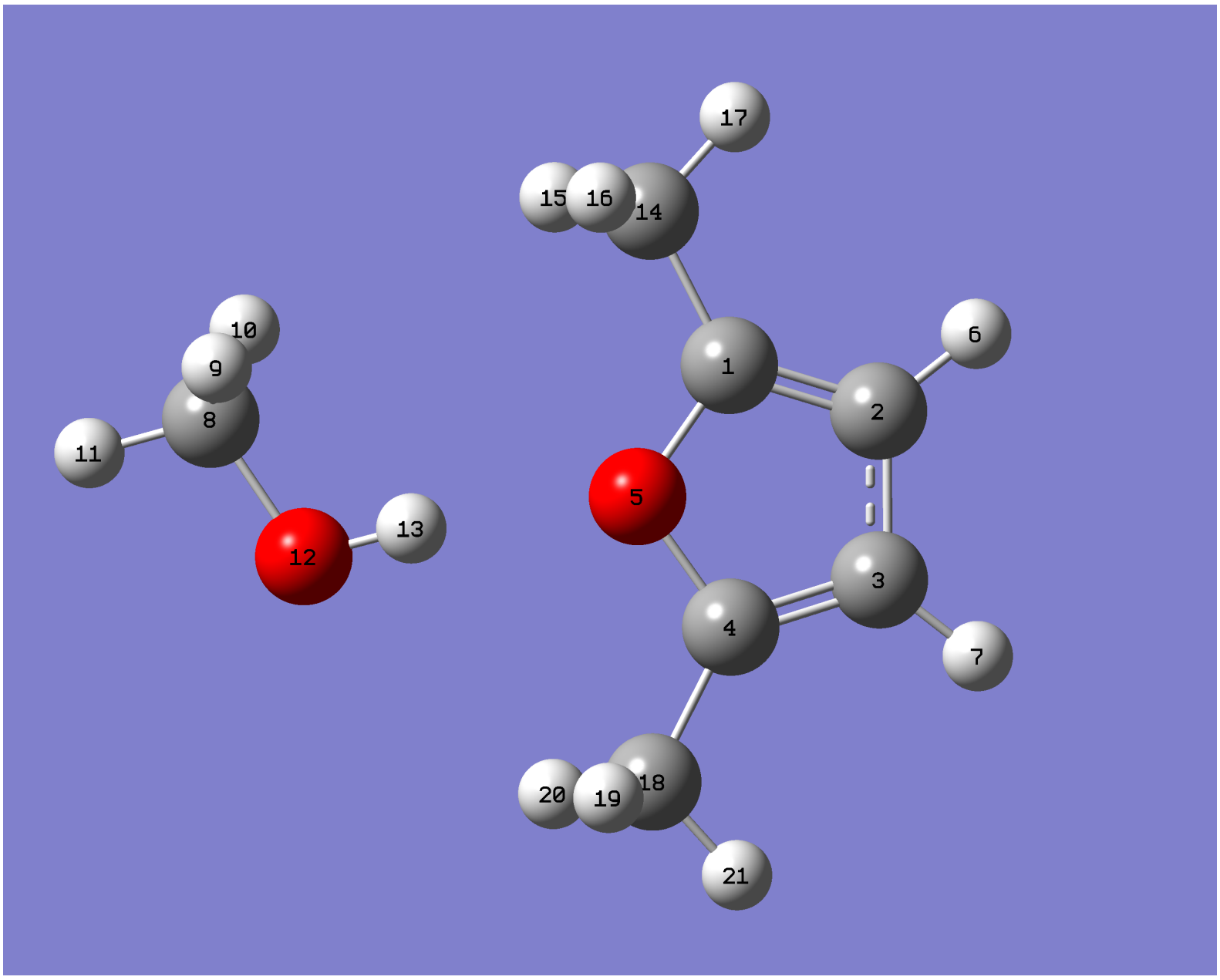

Figure S21: OH-bonded methanol – 2,5-dimethylfuran transition state in-plane structure with high energy.

Table S21: OH-bonded methanol – 2,5-dimethylfuran high-energy transition state

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							0.9066580	1.1813690	0.0478900
2	C	1			1.3601749			2.2092770	0.9268800	-0.2495910
3	C	2	1		1.4386517	106.8966344		2.3665620	-0.5031480	-0.2493640
4	C	3	2	1	1.3603463	106.9529127	-0.0882360	1.1512040	-1.0358240	0.0501410
5	O	1	2	3	1.3774302	109.0916879	0.1745968	0.2461610	-0.0124920	0.2369760
6	H	2	1	5	1.0783279	125.7564509	-179.8922197	2.9670700	1.6682970	-0.4466740
7	H	3	2	1	1.0782298	127.3274681	179.9664388	3.2676090	-1.0618240	-0.4457690
8	C	5	1	2	3.7066919	113.5299070	-160.0794490	-3.4349240	0.2634470	-0.0992320
9	H	8	5	1	1.0964212	86.7159765	-77.2409102	-3.4302930	0.7045250	0.9045450
10	H	8	5	1	1.0967694	85.8291039	31.8008137	-3.2285000	1.0534280	-0.8315040
11	H	8	5	1	1.0896891	153.8671450	156.0539092	-4.4316600	-0.1308180	-0.2954330
12	O	8	5	1	1.4179635	46.6013252	157.8190384	-2.5248090	-0.8181710	-0.2106490
13	H	12	8	5	0.9639189	108.0005418	1.6838615	-1.6401200	-0.4833610	-0.0252650
14	C	1	2	3	1.4856952	134.3991945	-179.9031802	0.0982730	2.4182240	0.2027890
15	H	14	1	2	1.0936520	111.3324548	119.2606004	-0.7225350	2.4500740	-0.5192460
16	H	14	1	2	1.0933965	111.3038860	-120.2149712	-0.3315770	2.4888540	1.2056630
17	H	14	1	2	1.0901935	109.5220169	-0.4203311	0.7315370	3.2902930	0.0384900
18	C	4	3	2	1.4859055	134.5494915	179.9257667	0.6290100	-2.4180300	0.2074150
19	H	18	4	3	1.0932208	111.2396550	117.6239675	0.2679180	-2.5916270	1.2245720
20	H	18	4	3	1.0929048	111.2386537	-122.3135744	-0.2017540	-2.6076480	-0.4769220
21	H	18	4	3	1.0901928	109.4166600	-2.2205744	1.4251170	-3.1323890	-0.0033580

S1.3.4 2,5-dimethylfuran OH low-energy TS OloTS

up to table of contents

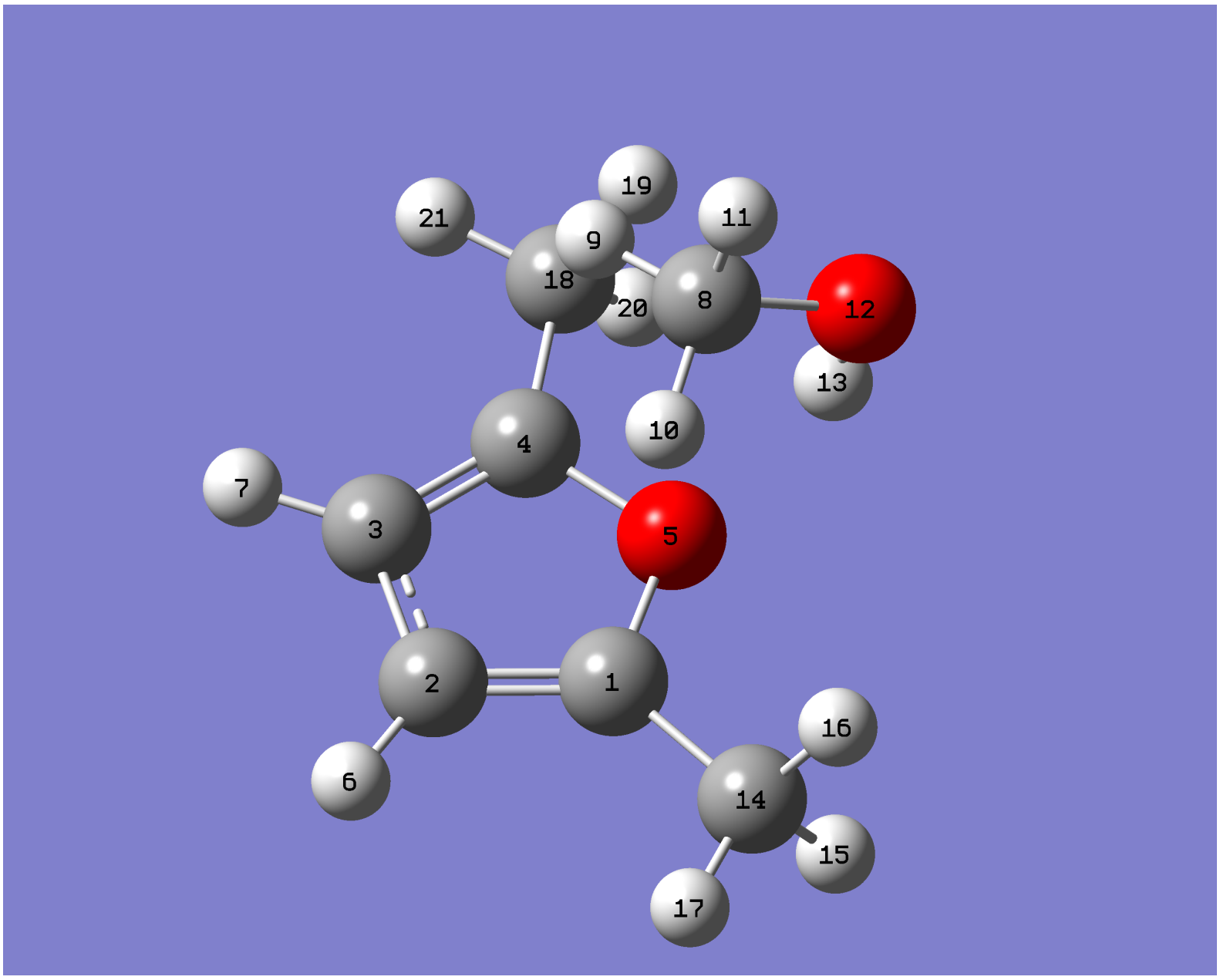

Figure S22: OH-bonded methanol – 2,5-dimethylfuran transition state in-plane structure with low energy.

Table S22: OH-bonded methanol – 2,5-dimethylfuran low-energy transition state

#	*N*	ref atom A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-0.8376710	-1.1145970	-0.1322450
2	C	1			1.3605869			-1.6490410	-0.7192530	0.8858800
3	C	2	1		1.4385100	106.8919583		-1.6490390	0.7192570	0.8858800
4	C	3	2	1	1.3605863	106.8919770	0.0000000	-0.8376690	1.1145990	-0.1322450
5	O	1	2	3	1.3783076	109.1416378	-0.0848133	-0.3338620	0.0000000	-0.7675260
6	H	2	1	5	1.0783558	125.7622200	179.8797120	-2.1837470	-1.3734090	1.5559700
7	H	3	2	1	1.0783559	127.3457739	179.9637480	-2.1837440	1.3734140	1.5559700
8	C	5	1	2	3.2518504	92.7271998	93.8924838	2.3691100	-0.0000030	1.0403660
9	H	8	5	1	1.0958503	75.9768775	-110.7711071	1.8240030	0.8887780	1.3777300
10	H	8	5	1	1.0958503	75.9769807	2.6598804	1.8240040	-0.8887850	1.3777290
11	H	8	5	1	1.0895903	171.4904811	125.9446867	3.3544560	-0.0000030	1.5054470
12	O	8	5	1	1.4213267	64.4549958	125.9443528	2.5726110	-0.0000020	-0.3663170
13	H	12	8	5	0.9628907	107.1310972	0.0000000	1.7025300	-0.0000020	-0.7787700
14	C	1	2	3	1.4856966	134.4632259	179.6853617	-0.4045490	-2.4315570	-0.6663950
15	H	14	1	2	1.0931951	111.2059268	119.0957239	-0.7142990	-2.5573760	-1.7072120
16	H	14	1	2	1.0935996	111.2256789	-120.6431754	0.6831140	-2.5374270	-0.6246720
17	H	14	1	2	1.0902181	109.5229579	-0.7476609	-0.8523620	-3.2299880	-0.0743250
18	C	4	3	2	1.4856969	134.4632479	-179.6853228	-0.4045430	2.4315580	-0.6663950
19	H	18	4	3	1.0935983	111.2256956	120.6431095	0.6831190	2.5374250	-0.6246720
20	H	18	4	3	1.0931952	111.2059185	-119.0957615	-0.7142930	2.5573780	-1.7072120
21	H	18	4	3	1.0902184	109.5229166	0.7475429	-0.8523550	3.2299900	-0.0743250

S1.3.5 2,5-dimethylfuran TS for OH-π conversion

up to table of contents

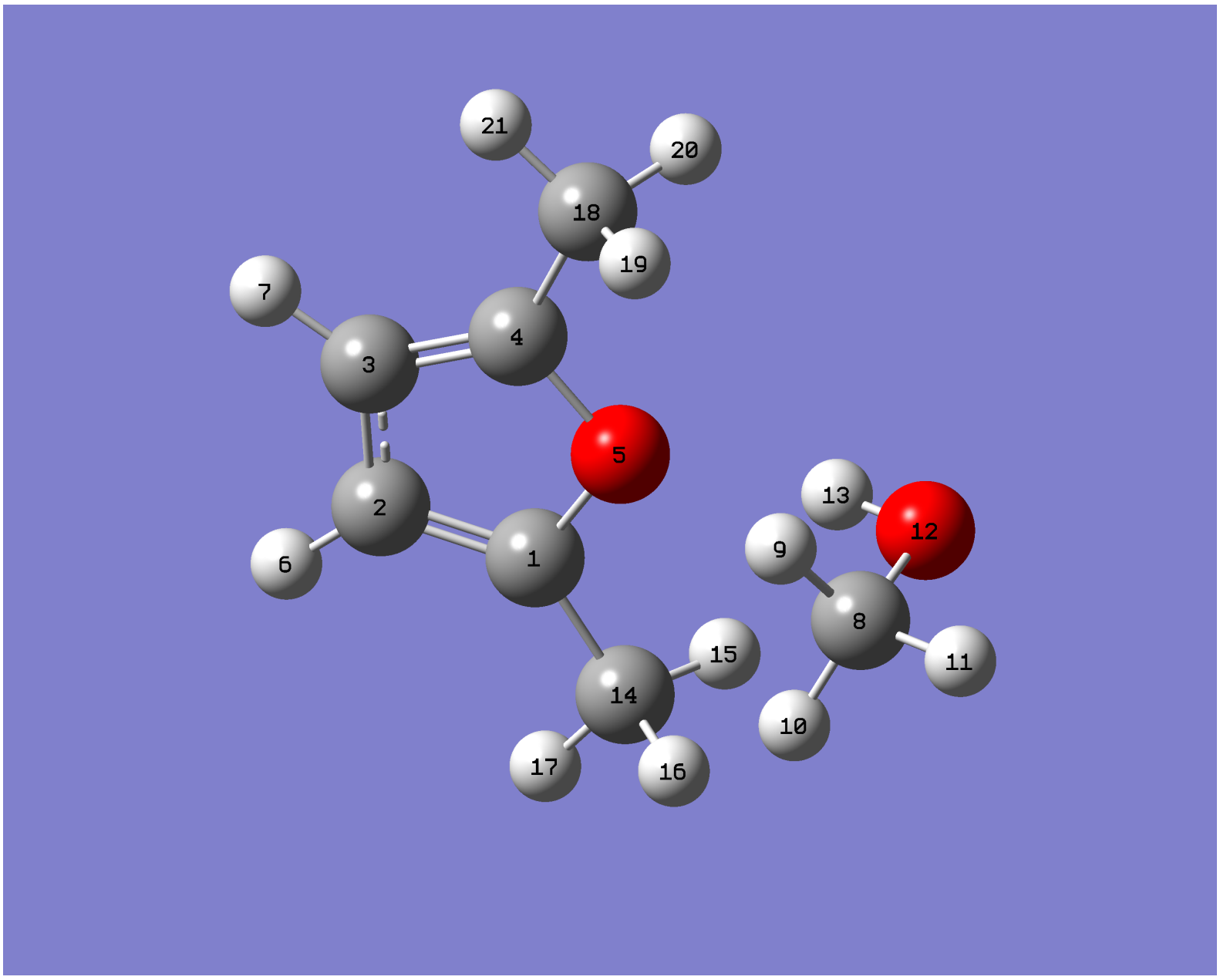

Figure S23: Methanol – 2,5-dimethylfuran transition state connecting OH- and π-bonded structure.

Table S23: Methanol – 2,5-dimethylfuran transition state connecting OH- and π-bonded structure.

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-0.9661770	-1.1151340	-0.0596060
2	C	1			1.3604298			-2.1886840	-0.7193430	0.3871550
3	C	2	1		1.4386870	106.9136928		-2.1886840	0.7193440	0.3871550
4	C	3	2	1	1.3604295	106.9136525	0.0000000	-0.9661770	1.1151340	-0.0596060
5	O	4	3	2	1.3776052	109.0418758	0.0341848	-0.2067150	0.0000000	-0.3379760
6	H	2	1	5	1.0782723	125.7518232	179.8947637	-2.9943130	-1.3732790	0.6804140
7	H	3	2	1	1.0782723	127.3344410	179.9274788	-2.9943130	1.3732800	0.6804140
8	C	5	4	3	3.3748597	116.6920067	-133.9347074	2.9654120	0.0000000	0.8141040
9	H	8	5	4	1.0965790	79.0321232	9.2358922	2.5623500	0.8896070	1.3127280
10	H	8	5	4	1.0965798	79.0321314	120.6872789	2.5623500	-0.8896080	1.3127280
11	H	8	5	4	1.0897370	166.4252332	-115.0384294	4.0483880	0.0000000	0.9353050
12	O	8	5	4	1.4181498	59.1741067	-115.0384294	2.6980860	0.0000000	-0.5786220
13	H	12	8	5	0.9637004	107.2008666	0.0000000	1.7402710	0.0000000	-0.6849650
14	C	1	2	3	1.4857191	134.4911240	-179.8964391	-0.3208120	-2.4320530	-0.2974920
15	H	14	1	2	1.0930530	111.2345835	120.5873744	-0.0176190	-2.5414380	-1.3419410
16	H	14	1	2	1.0933514	111.3771284	-119.1871332	0.5705320	-2.5569880	0.3232450
17	H	14	1	2	1.0901729	109.4945900	0.6861274	-1.0229600	-3.2302320	-0.0558820
18	C	4	3	2	1.4857191	134.4910837	179.8964392	-0.3208120	2.4320530	-0.2974920
19	H	18	4	3	1.0933514	111.3771284	119.1871331	0.5705320	2.5569880	0.3232450
20	H	18	4	3	1.0930539	111.2345731	-120.5873622	-0.0176190	2.5414380	-1.3419420
21	H	18	4	3	1.0901722	109.4946262	-0.6861089	-1.0229590	3.2302320	-0.0558820

S1.3.6 2,5-dimethylfuran π-bonded conformation PI

up to table of contents

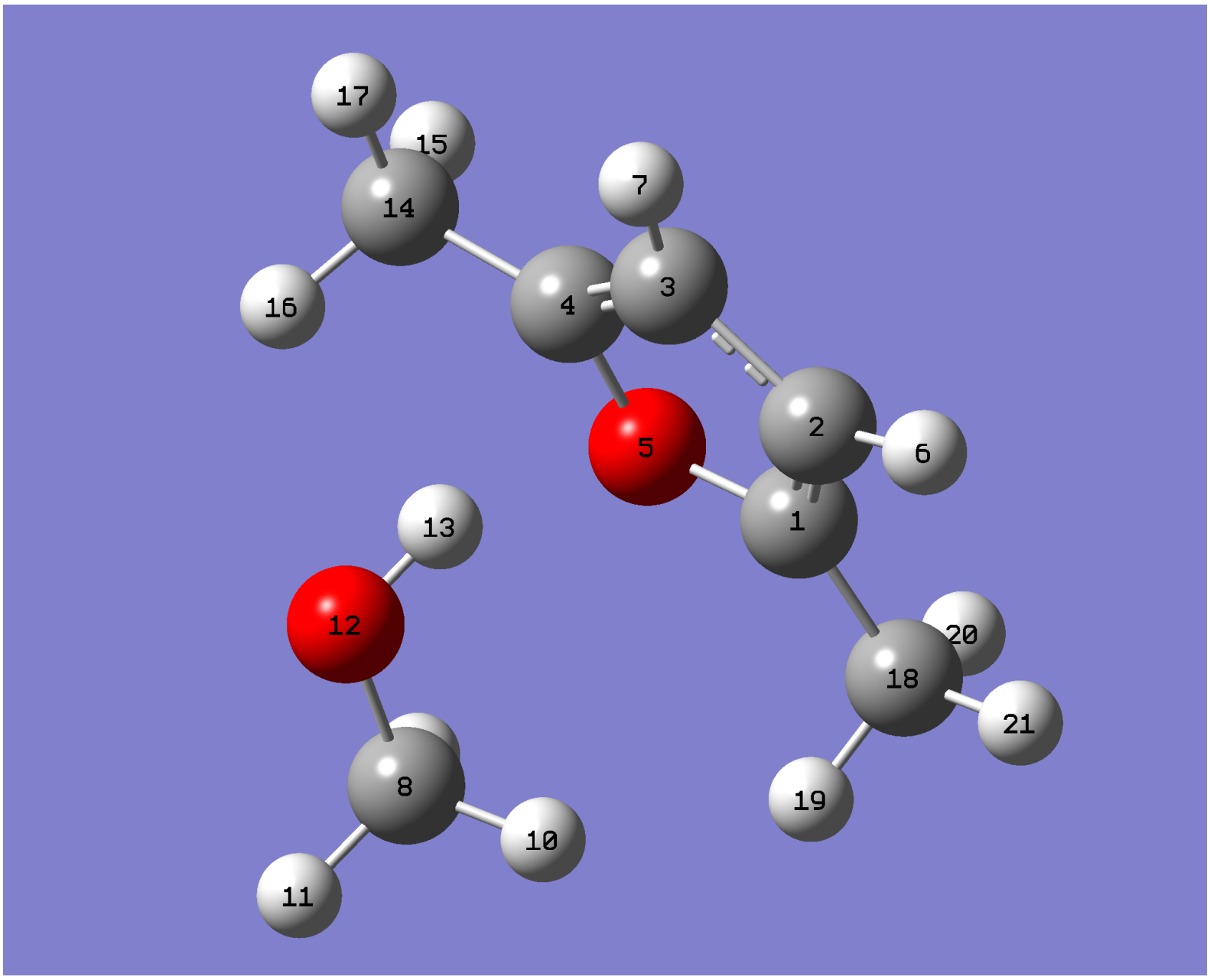

Figure S24: π-bonded methanol – 2,5-dimethylfuran conformation

Table S24: π-bonded methanol – 2,5-dimethylfuran structure.

#	N	ref atom A	B	C	Bond	Angle	Dihedral	X	Y	Z
1	C							1.4084540	-0.2559170	0.0363630
2	C	1			1.3624209			1.1181360	0.0946150	1.3205100
3	C	2	1		1.4389998	106.6407046		0.1351340	1.1431150	1.2492700
4	C	3	2	1	1.3647028	106.6734863	0.0433847	-0.1092340	1.3613870	-0.0755150
5	O	4	3	2	1.3718076	109.2881755	0.0812607	0.6621650	0.5097910	-0.8249040
6	H	2	1	5	1.0783196	125.9592053	-179.9797918	1.5518360	-0.3373270	2.2082620
7	H	3	2	1	1.0786861	127.4864734	-179.2761529	-0.3210120	1.6722570	2.0711600
8	C	5	4	3	3.4623829	90.9661560	81.3133913	-1.6046440	-2.0624740	-0.3420740
9	H	8	5	4	1.0954403	46.1463997	126.9990358	-1.1458560	-1.6116550	-1.2287900
10	H	8	5	4	1.0957468	88.9551655	-115.3911746	-0.8347510	-2.6098170	0.2132110
11	H	8	5	4	1.0897580	154.0723923	110.9445227	-2.3677730	-2.7699270	-0.6656740
12	O	8	5	4	1.4209064	82.6496335	-3.1604595	-2.2542520	-1.0931280	0.4686990
13	H	12	8	5	0.9633190	107.8239533	-25.5202934	-1.5871550	-0.4682900	0.7729070
14	C	4	3	2	1.4854381	133.9968948	178.9050829	-1.0134720	2.2739230	-0.8212750
15	H	14	4	3	1.0929042	111.0986742	122.4850740	-0.4503840	2.9115620	-1.5074150
16	H	14	4	3	1.0929690	110.9670964	-117.0623543	-1.7461780	1.7089890	-1.4031450
17	H	14	4	3	1.0901514	109.5681011	2.5151067	-1.5511470	2.9101810	-0.1180600
18	C	1	2	3	1.4854232	134.0347047	-179.7967097	2.3190710	-1.2541460	-0.5807250
19	H	18	1	2	1.0933508	111.1653934	119.4839245	1.7623510	-1.9770320	-1.1831490
20	H	18	1	2	1.0930407	111.1740182	-120.3023066	3.0532060	-0.7704470	-1.2302010
21	H	18	1	2	1.0902801	109.6007882	-0.4006180	2.8528880	-1.7948180	0.2012110

S1.3.7 2,5-dimethylfuran π-bonded low TS PiloTS

up to table of contents

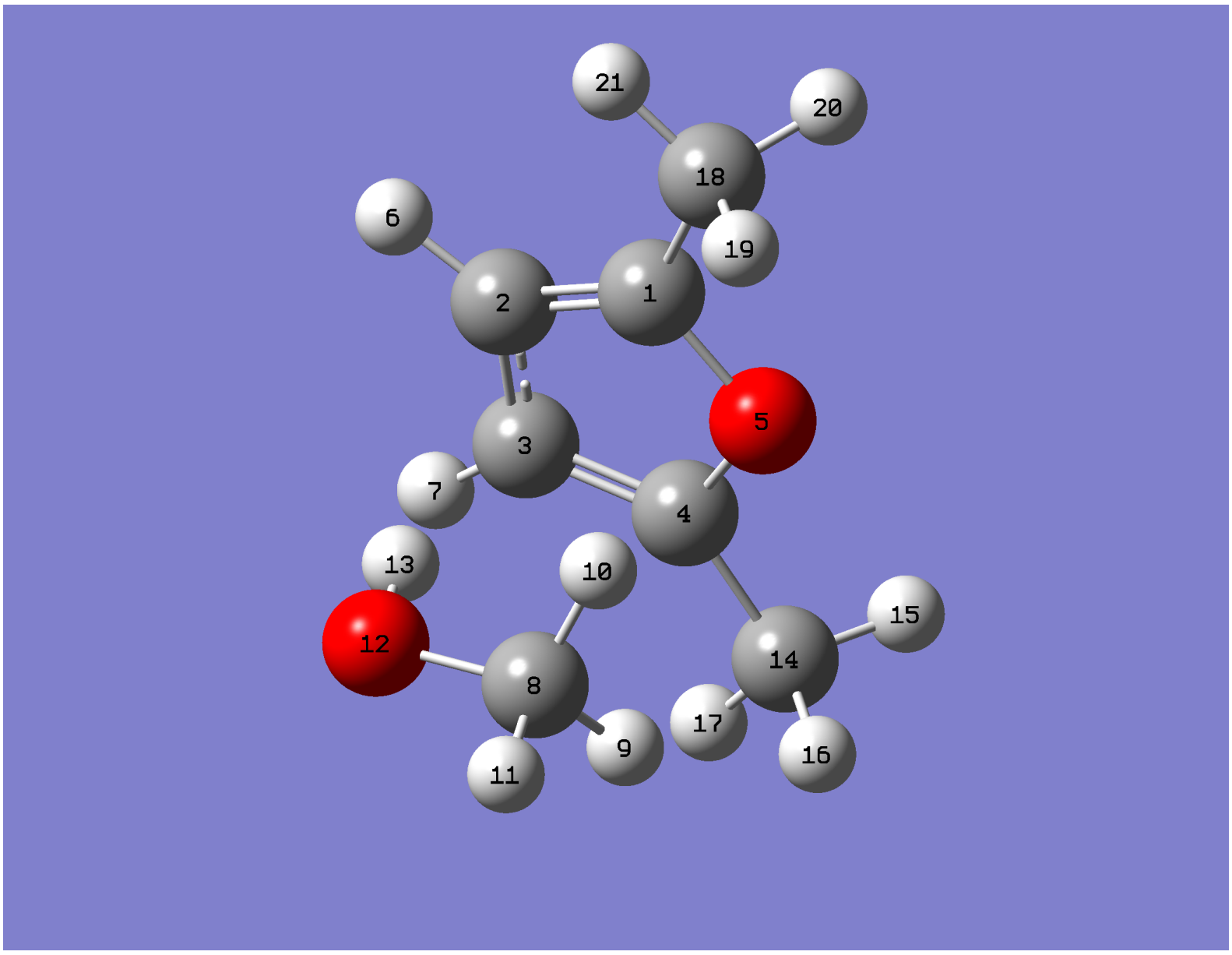

Figure S25: π-bonded methanol – 2,5-dimethylfuran transition state of lowest energy.

Table S25: π-bonded methanol – 2-methylfuran transition state of lowest energy.

		ref atom								
#	*N*	A	B	C	Bond	Angle	Dihedral	*X*	*Y*	*Z*
1	C							-0.8588720	1.1099270	0.0155860
2	C	1			1.3636815			-0.7285660	0.7196550	1.3157150
3	C	2	1		1.4393070	106.6300326		-0.7285660	-0.7196520	1.3157160
4	C	3	2	1	1.3636815	106.6300850	0.0000000	-0.8588730	-1.1099270	0.0155880
5	O	4	3	2	1.3718541	109.3646926	-0.0332339	-0.9400250	-0.0000010	-0.7865730
6	H	2	1	5	1.0784835	125.8853845	-179.6535609	-0.6479730	1.3759520	2.1677160
7	H	3	2	1	1.0784838	127.4836794	-179.6802195	-0.6479740	-1.3759470	2.1677190
8	C	5	4	3	3.4673901	85.9978095	84.5270699	2.5267900	-0.0000020	-0.7234240
9	H	8	5	4	1.0956577	62.7026589	59.8061335	2.0316090	-0.8894380	-1.1285970
10	H	8	5	4	1.0956580	62.7026336	-168.2031923	2.0316090	0.8894330	-1.1286000
11	H	8	5	4	1.0896987	161.2528371	125.8014518	3.5648830	-0.0000030	-1.0547940
12	O	8	5	4	1.4194741	91.7171546	-54.1985146	2.5434780	0.0000000	0.6959520
13	H	12	8	5	0.9627137	107.4534742	0.0000000	1.6285450	0.0000010	0.9954770
14	C	4	3	2	1.4856022	133.8955497	-179.6833916	-0.9326310	-2.4304540	-0.6610080
15	H	14	4	3	1.0931522	111.1587174	118.6042574	-1.8843210	-2.5528600	-1.1847300
16	H	14	4	3	1.0930596	111.2483696	-121.1302009	-0.1291560	-2.5459180	-1.3930430
17	H	14	4	3	1.0901579	109.5520791	-1.2873467	-0.8406490	-3.2253620	0.0793330
18	C	1	2	3	1.4856031	133.8955688	179.6834275	-0.9326290	2.4304530	-0.6610140
19	H	18	1	2	1.0930593	111.2483498	121.1302395	-0.1291540	2.5459140	-1.3930490
20	H	18	1	2	1.0931522	111.1587428	-118.6041848	-1.8843190	2.5528590	-1.1847360
21	H	18	1	2	1.0901580	109.5520775	1.2873507	-0.8406470	3.2253630	0.0793250

S1.3.8 2,5-dimethylfuran π-bonded high TS PihiTS

up to table of contents

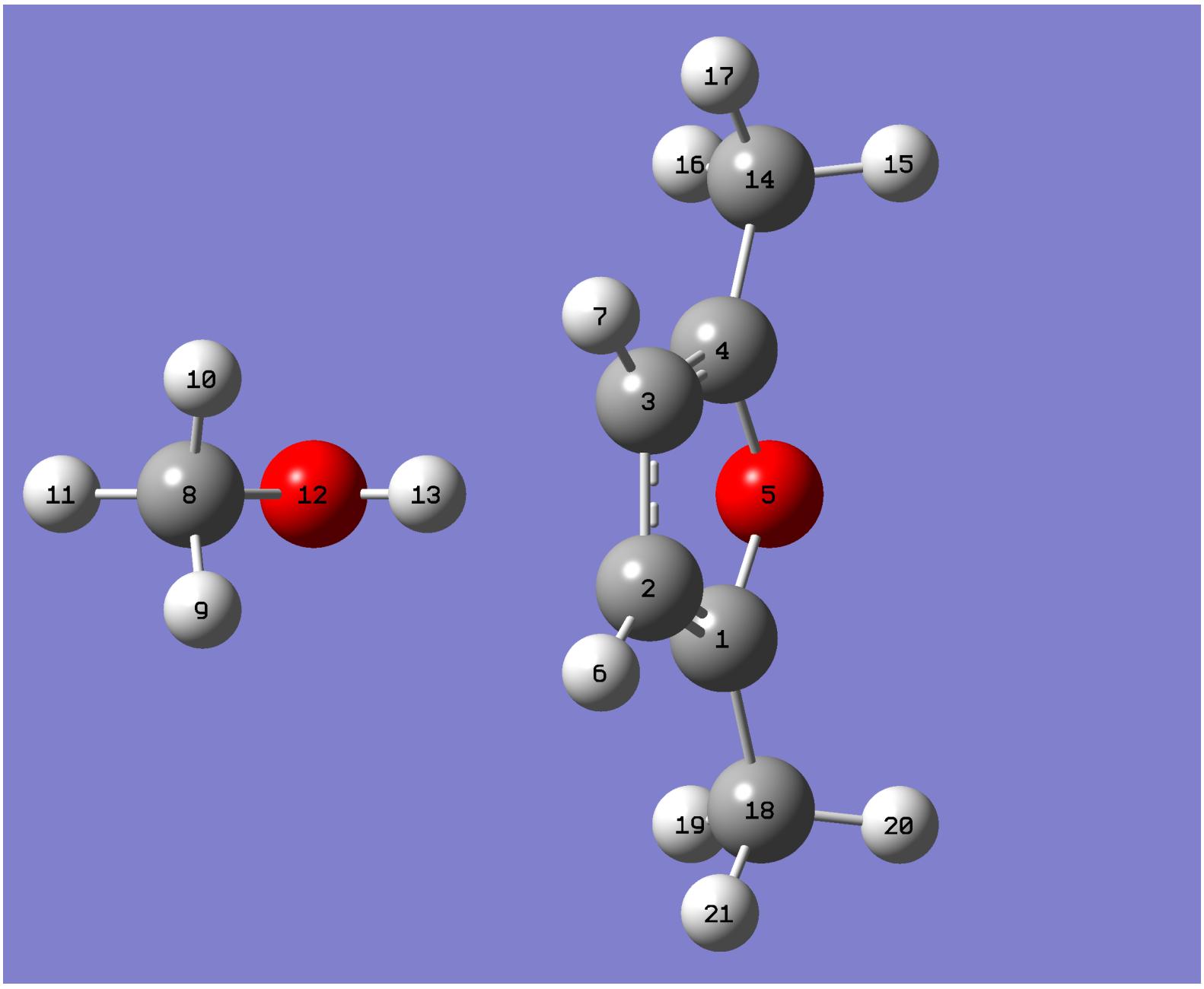

Figure S26: π-bonded methanol – 2,5-dimethylfuran transition state of highest energy.

Table S26: π-bonded methanol – 2,5-dimethylfuran transition state of highest energy.

#	N	ref atom A	B	C	Bond	Angle	Dihedral	X	Y	Z
1	C							0.9371660	-1.1108940	0.1157600
2	C	1			1.3635608			0.3652620	-0.7194610	1.2900700
3	C	2	1		1.4389210	106.6824298		0.3652620	0.7194600	1.2900700
4	C	3	2	1	1.3635611	106.6824700	0.0000000	0.9371660	1.1108940	0.1157600
5	O	4	3	2	1.3728594	109.3013381	0.0540367	1.2892500	0.0000000	-0.6099770
6	H	2	1	5	1.0784231	125.8474437	-179.8952851	-0.0073200	-1.3755140	2.0606370
7	H	3	2	1	1.0784238	127.4698823	-179.8378376	-0.0073200	1.3755130	2.0606380
8	C	3	2	1	3.7866960	79.0474045	97.6807985	-3.1647240	0.0000000	0.1236040
9	H	8	3	2	1.0959427	84.1963677	31.5993795	-3.0731340	-0.8906940	0.7555580
10	H	8	3	2	1.0959427	65.7984616	145.1435330	-3.0731340	0.8906940	0.7555580
11	H	8	3	2	1.0896164	167.2642981	-148.8965503	-4.1536530	0.0000000	-0.3338710
12	O	8	3	2	1.4196771	66.9030062	-85.2658769	-2.2177800	0.0000000	-0.9341200
13	H	12	8	3	0.9617065	107.0718897	11.9204651	-1.3445190	0.0000000	-0.5312620
14	C	4	3	2	1.4854498	134.0510247	179.2182253	1.2230800	2.4299790	-0.5045860
15	H	14	4	3	1.0929972	111.1277075	121.2951477	2.2910200	2.5477850	-0.7052570
16	H	14	4	3	1.0929813	111.0148387	-118.4037792	0.6861270	2.5432230	-1.4498190
17	H	14	4	3	1.0902397	109.5691850	1.3893535	0.9076410	3.2266210	0.1695670
18	C	1	2	3	1.4854503	134.0510151	-179.2182021	1.2230800	-2.4299790	-0.5045870
19	H	18	1	2	1.0929812	111.0148204	118.4037786	0.6861270	-2.5432220	-1.4498200
20	H	18	1	2	1.0929972	111.1277089	-121.2951499	2.2910200	-2.5477850	-0.7052580
21	H	18	1	2	1.0902397	109.5691540	-1.3893750	0.9076410	-3.2266210	0.1695660

S2 Method details

Geometries, 1D-scans and frequencies were obtained at B2PLYP-D3/6-311++g(d,p) level throughout. Stationary points, *i.e.* minima and transition states (TSs), were optimized with the standard schemes within the gaussian09.d01 software [1]. An "ultra-ultrafine" density functional theory (DFT) integration grid of 199 radial shells ands and 974 angular points per atom was used and self-consistent field (SCF) convergence criteria were set to $10^{11} E_\mathrm{h}$. Only for the methanol-2,5-dimethylfuran OH-bonded dimer this convergence couldn't be achieved but was set to $10^{9} E_\mathrm{h}$ at least.

S3 Electronic energies

S3.1 Method details

Single-point energies (SPEs) were calculated using the ORCA 4.0.1 version for linux x86 64bit machines [2]. We employed two different families of basis sets: Ahlrichs basis sets def2-TZVPP and def2-QZVPP have been used with the corresponding auxiliary bases with suffix /c and extrapolated according to the formula provided by Liakos *et al.* [3, 4]:

$$E_\mathrm{CBS} = \frac{E_\mathrm{HF,QZ}\exp(-\alpha\sqrt{3}) - E_\mathrm{HF,TZ}\exp(-\alpha\sqrt{4})}{\exp(-\alpha\sqrt{3}) - \exp(-\alpha\sqrt{4})} + \frac{3^\beta E_\mathrm{CC,TZ} - 4^\beta E_\mathrm{CC,QZ}}{3^\beta - 4^\beta} \quad (1)$$

The actual values of α and β are "constants depending on the basis sets" and discussed in the earlier work by Neese *et al.* [3]. For triple- to quadruple-ζ basis set extrapolation of def2-Ahlrichs bases, the parameters read $\alpha = 7.88$ and $\beta = 2.97$.

For augmented Dunning basis sets, for double- and triple-ζ extrapolation we employed $\alpha = 4.30$ and $\beta = 2.51$[2] and for triple- and quadruple extrapolation $\alpha = 5.79$ and $\beta = 3.05$. For all delocalized pair natural orbital approximated (DLPNO) calculations, TightSCF and TightPNO settings were used[3] and were performed on 8 cores and 8 GB per core maximum RAM (openmpi-2.0.2 parallelization). In previous versions of gaussview, B2PLYP energies were incorrectly displayed, i.e. just the SCF energies were shown. We therefore created a perl script to replace B2PLYP SCF energies by the final perturbation-corrected energies. This is why most log filenames carry an "_repl" extension – they contain replaced energies.

S3.2 Methanol – furan system

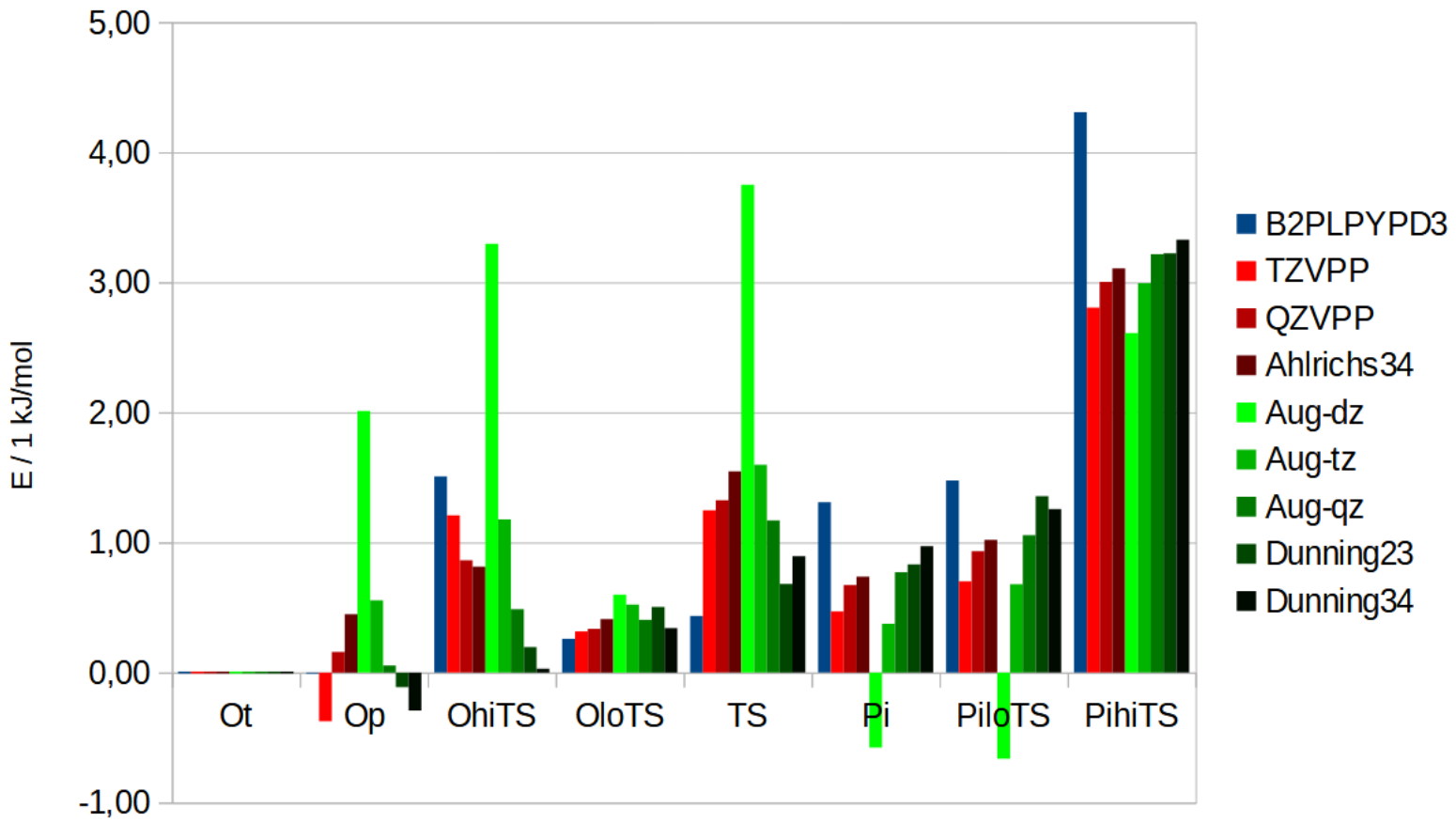

Figure S27: DLPNO-CCSD(T) energies with various basis sets for all stationary points of the methanol - furan dimer.

up to table of contents

[2] where in the equation QZ must be replaced by TZ and TZ by DZ and 4 by 3 and 3 by 2.
[3] we also set the mdci maxiter keyword to 100

Table S27: Methanol – furan dimer torsional angles, corresponding normal mode vibrational frequency, and energies.

	Ot	Op	OhiTS	OloTS	TS	Pi	PiloTS	PihiTS
$\theta_{\mathrm{C-O-O-C}}$	-37.69084	-95.11377	0=180	59.25	-85.6796	165.22427	-118.99142	57.12118
ν_{lowest}	31.96	21.97	-38.34	-32.96	-18.33	19.32	-17.58	-49.98
				Energies in hartree/particle				
B2PLYP	-345.52690678352	-345.526909659779	-345.52633201868	-345.52680783815	-345.52674103266	-345.526407254569	-345.52634403578	-345.52526537014
TZVPP	-345.200355306	-345.200497707	-345.199894917	-345.200234786	-345.199879932	-345.200176161	-345.200088093	-345.199286933
QZVPP	-345.297465936	-345.297405401	-345.297137413	-345.297337519	-345.296961043	-345.29720956	-345.297110529	-345.296322189
Ahlrichs34	-345.35996490384	-345.35979376554	-345.35965474943	-345.35980840438	-345.35937563287	-345.35968394696	-345.35957629441	-345.35878151664
aug-dz	-344.911130756	-344.910364607	-344.909875195	-344.910902306	-344.909702152	-344.911350329	-344.911382916	-344.910136297
aug-tz	-345.21802434	-345.217812707	-345.217575705	-345.217825206	-345.217415327	-345.217881328	-345.217765354	-345.216883541
aug-qz	-345.306018987	-345.305998128	-345.305833148	-345.305864669	-345.305573266	-345.305724786	-345.305616721	-345.304794117
aug-(d,t)z	-345.37274207	-345.372784713	-345.372667091	-345.372549557	-345.372482297	-345.372425032	-345.372225274	-345.371514152
aug-(t,q)z	-345.359386929	-345.359498098	-345.359375601	-345.359256648	-345.359046067	-345.359016437	-345.358908246	-345.358119718
aug-5z	-345.333138088	-345.333136014				-345.332827055		
				Energies with respect to Ot in kJ/mol				
B2PLYP	0.00	-0.01	1.51	0.26	0.44	1.31	1.48	4.31
TZVPP	0.00	-0.37	1.21	0.32	1.25	0.47	0.70	2.81
QZVPP	0.00	0.16	0.86	0.34	1.33	0.67	0.93	3.00
Ahlrichs34	0.00	0.45	0.81	0.41	1.55	0.74	1.02	3.11
aug-dz	0.00	2.01	3.30	0.60	3.75	-0.58	-0.66	2.61
aug-tz	0.00	0.56	1.18	0.52	1.60	0.38	0.68	3.00
aug-qz	0.00	0.05	0.49	0.41	1.17	0.77	1.06	3.22
aug-(d,t)z	0.00	-0.11	0.20	0.51	0.68	0.83	1.36	3.22
aug-(t,q)z	0.00	-0.29	0.03	0.34	0.89	0.97	1.26	3.33
aug-5z	0.00	0.01				0.82		

S3.3 Methanol – 2-methylfuran system

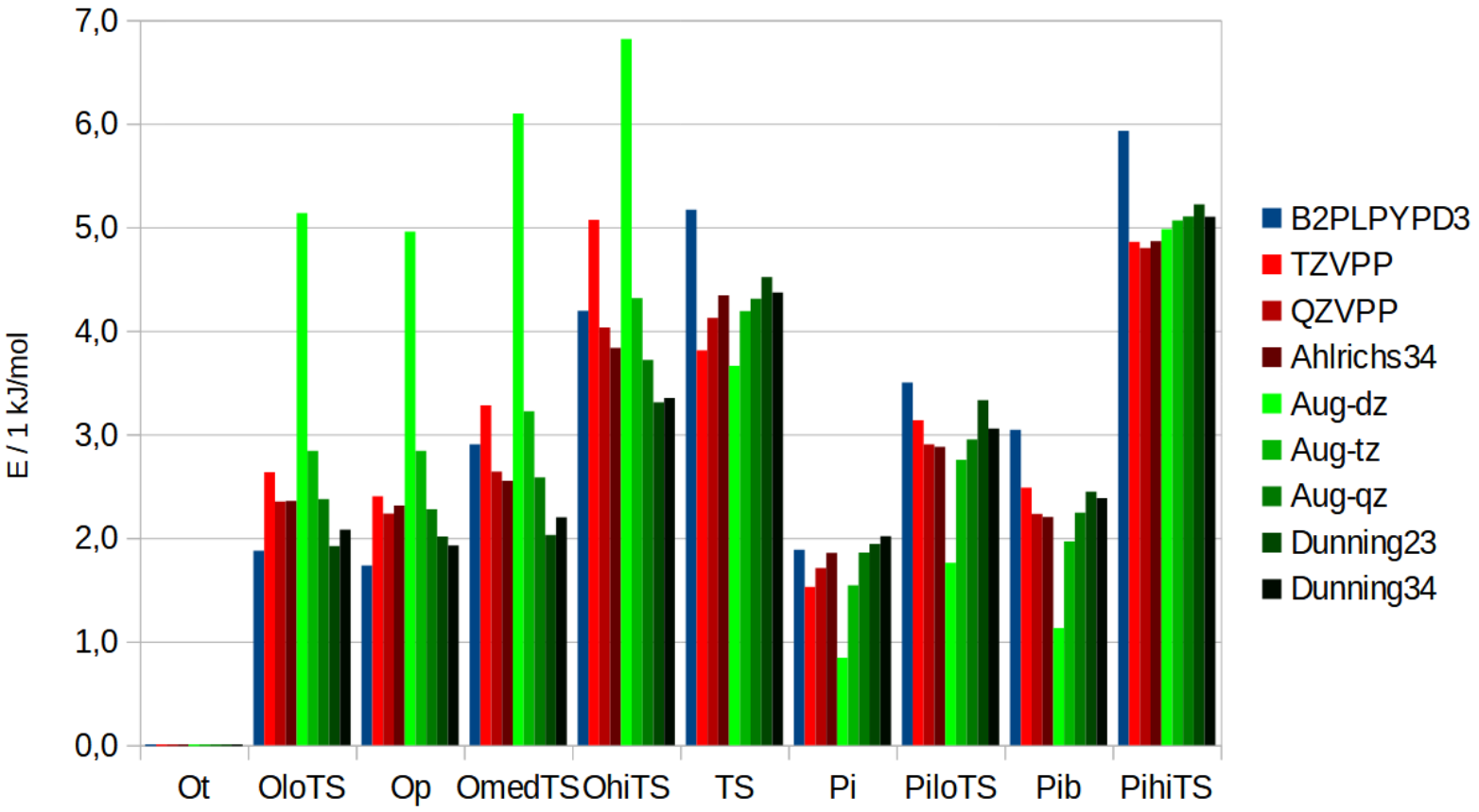

Figure S28: DLPNO-CCSD(T) energies with various basis sets for all stationary points of the methanol - 2-methylfuran dimer.

up to table of contents

S3.4 Methanol – 2,5-dimethylfuran system

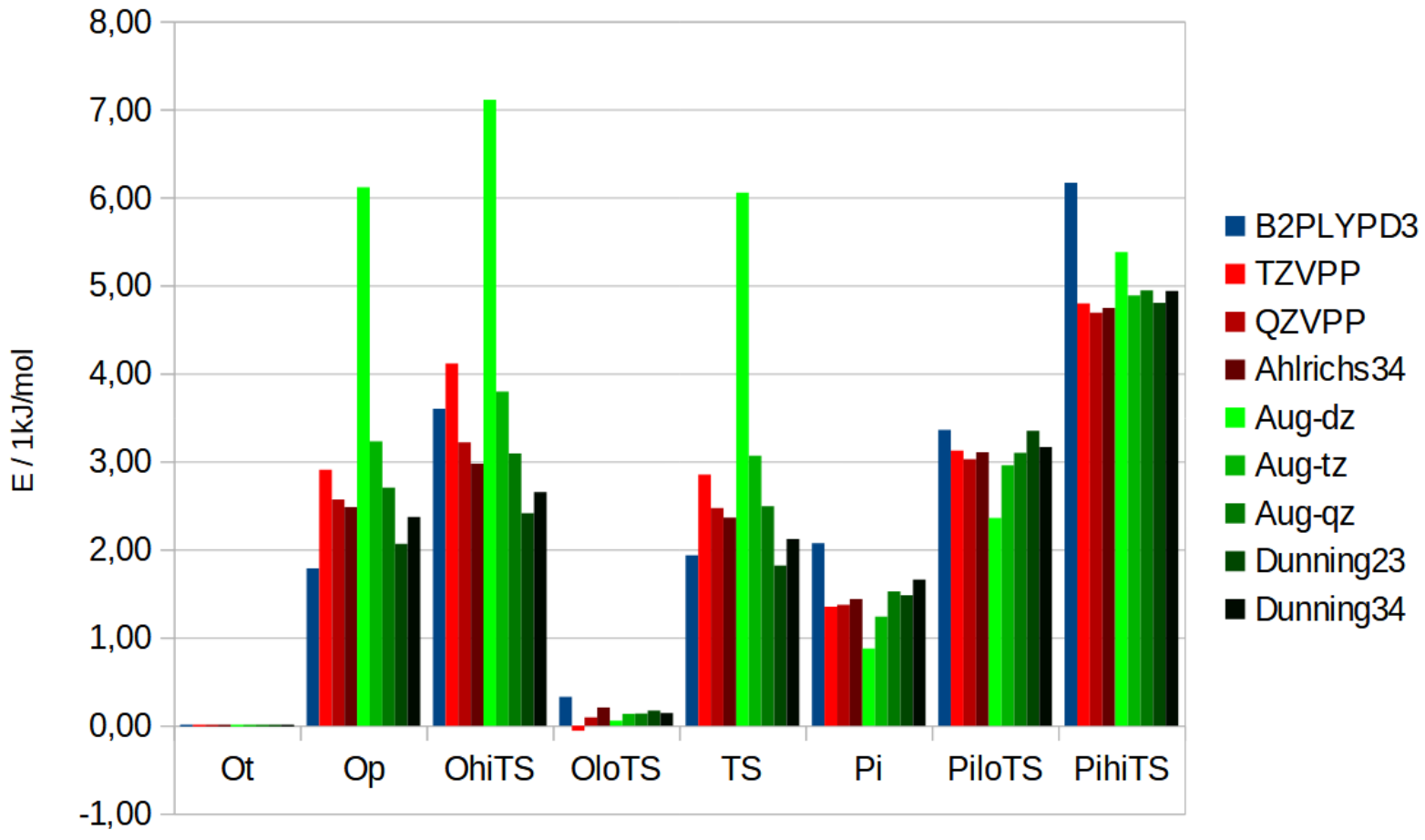

Figure S29: DLPNO-CCSD(T) energies with various basis sets for all stationary points of the methanol - 2,5-dimethylfuran dimer.

up to table of contents

S4 Hindered rotor results

The TAMkin [5] Python library version 1.2.6 is licensed under the GNU General Public License v3.0 and can be obtained via pip, conda, or manually from the project's GitHub page.

The TAMkinTools code developed in this study is available under MIT license on GitLab of RWTH Aachen University at `https://git.rwth-aachen.de/Wassja.Kopp/tamkintools`. The version released for this study will be committed to a separate publication branch.

Table S28: Methanol – 2-methylfuran torsional angles, corresponding normal mode vibrational frequency, and energies.

	Ot	OloTS	Op	OmedTS	OhiTS	TS	Pi	PiloTS	Pib	PihiTS
$\theta_{\mathrm{C-O-O-C}}$	40.04135	-77.19415	-104.87742	-45.26506	-178.4621	-144.31447	65.75423	1.20334	33.81733	-150.69257
ν_{lowest}	35.41	-21.85	12.94	-23.68	-41.82	-39.385	31.30	-28.90	32.75	-26.71
Energies in hartree/particle										
B2PLYP	-384.81648165959	-384.81576671896	-384.81582091994	-384.81537554232	-384.81488430883	-384.81451212381	-384.81576351502	-384.81514792965	-384.81532179986	-384.81422212591
TZVPP	-384.449591006	-384.448586744	-384.448676268	-384.448341888	-384.447659513	-384.448139217	-384.449009446	-384.448395768	-384.448643923	-384.447739821
QZVPP	-384.557625353	-384.556729749	-384.556774392	-384.55661931	-384.556090057	-384.556054455	-384.556974008	-384.556519563	-384.556775117	-384.555796708
Ahlrichs34	-384.62724748385	-384.62634998061	-384.62636613859	-384.62627568563	-384.62578646773	-384.6255935791	-384.62654048342	-384.62614983627	-384.62640817097	-384.62539467288
aug-dz	-384.126160805	-384.124204166	-384.124272448	-384.12383781	-384.123564056	-384.124765515	-384.125839625	-384.125490724	-384.125730113	-384.124263812
aug-tz	-384.469758365	-384.468675853	-384.468676624	-384.468531069	-384.468114062	-384.468162795	-384.46917075	-384.468708839	-384.469009543	-384.467828916
aug-qz	-384.567142605	-384.566238186	-384.56627548	-384.566157869	-384.565725964	-384.565501449	-384.566434111	-384.566017584	-384.566287824	-384.565198961
aug-(d,t)z	-384.643255845	-384.642523226	-384.642488653	-384.642482901	-384.641994797	-384.641534909	-384.642516269	-384.641987506	-384.642323273	-384.641267391
aug-(t,q)z	-384.626237011	-384.625444292	-384.625502558	-384.625398939	-384.62495978	-384.624572571	-384.625468865	-384.625072937	-384.625329311	-384.624294298
Energies with respect to Ot in kJ/mol										
B2PLYP	0	1.88	1.73	2.90	4.19	5.17	1.89	3.50	3.05	5.93
TZVPP	0	2.64	2.40	3.28	5.07	3.81	1.53	3.14	2.49	4.86
QZVPP	0	2.35	2.23	2.64	4.03	4.12	1.71	2.90	2.23	4.80
Ahlrichs34	0	2.36	2.31	2.55	3.84	4.34	1.86	2.88	2.20	4.86
aug-dz	0	5.14	4.96	6.10	6.82	3.66	0.84	1.76	1.13	4.98
aug-tz	0	2.84	2.84	3.22	4.32	4.19	1.54	2.76	1.97	5.07
aug-qz	0	2.37	2.28	2.59	3.72	4.31	1.86	2.95	2.24	5.10
aug-(d,t)z	0	1.92	2.01	2.03	3.31	4.52	1.94	3.33	2.45	5.22
aug-(t,q)z	0	2.08	1.93	2.20	3.35	4.37	2.02	3.06	2.38	5.10

Table S29: Methanol – 2,5-dimethylfuran torsional angles, corresponding normal mode vibrational frequency, and energies.

	Ot	Op	OhiTS	OloTS	TS	Pi	PiloTS	PihiTS
$\theta_{\mathrm{C-O-O-C}}$	43.16909	-94.77078	156.00091	57.93	79.1	71.3838	15.1597	-160.09
ν_{lowest}	37.05	13.58	-31.82	-31.81	-21.12	34.11	-36.69	-64.71
Energies in hartree/particle								
B2PLYP	-424.10509159429	-424.10441120463	-424.10372117947	-424.10496701329	-424.104354305	-424.10430257468	-424.10381200814	-424.10274331964
TZVPP	-423.697755862	-423.696648709	-423.696188297	-423.697777935	-423.696669785	-423.697241964	-423.696566643	-423.695929061
QZVPP	-423.816865977	-423.815887413	-423.81563963	-423.816830489	-423.815924187	-423.816343776	-423.815712603	-423.815079121
(T.Q)ZVPP	-423.89364978186	-423.89270492917	-423.89251595878	-423.893571287405	-423.892749922679	-423.89310174332	-423.89246713815	-423.89184287869
aug-dz	-423.340313485	-423.337984665	-423.337606277	-423.340292068	-423.338007877	-423.339979591	-423.339415479	-423.338264072
aug-tz	-423.720475349	-423.719244838	-423.71902941	-423.720424144	-423.719308113	-423.720003355	-423.719348564	-423.718614411
aug-qz	-423.827355813	-423.826326136	-423.826178965	-423.827303442	-423.826406239	-423.826775235	-423.826174982	-423.825473293
aug-(d.t)z	-423.912653487	-423.911866556	-423.911734088	-423.912588110035	-423.911961259987	-423.912089084	-423.911377884	-423.910825034
aug-(t.q)z	-423.892236241	-423.891334125	-423.891226185	-423.892181331285	-423.891428188959	-423.891604354	-423.891031631	-423.890356551
Energies with respect to Ot in kJ/mol								
B2PLYP	0.00	1.79	3.60	0.33	1.94	2.07	3.36	6.17
TZVPP	0.00	2.91	4.12	-0.06	2.85	1.35	3.12	4.80
QZVPP	0.00	2.57	3.22	0.09	2.47	1.37	3.03	4.69
(T.Q)ZVPP	0.00	2.48	2.98	0.21	2.36	1.44	3.11	4.74
aug-dz	0.00	6.11	7.11	0.06	6.05	0.88	2.36	5.38
aug-tz	0.00	3.23	3.80	0.13	3.06	1.24	2.96	4.89
aug-qz	0.00	2.70	3.09	0.14	2.49	1.52	3.10	4.94
aug-(d.t)z	0.00	2.07	2.41	0.17	1.82	1.48	3.35	4.80
aug-(t.q)z	0.00	2.37	2.65	0.14	2.12	1.66	3.16	4.94

S4.1 Technical hints for working with TAMkin and TAMkinTools

We corrected the original rotor.py file of TAMkin for two issues: The first refers to lines 515 to 540 in the def potential(self). Here, we replace the line `deltas -= np.floor(deltas/a)*a` by `deltas -= (abs(np.floor(deltas/a))-0.5)*a` and `deltas = abs(deltas)`. The original version shifted the minimum to the right sometimes. The new version makes sure the correct minimum is taken.

The second issue is already corrected for in newer versions of TAMkin and refers to the construction of the design matrix near lines 250, 251. The old code reads: `ncos = min(dofmax, self.nmax/rotsym)` and this has to be adjusted to `ncos = min(dofmax, int(self.nmax/rotsym))`. This was coming from python2 where the "/" division returned an integer when both inputs were integers. In python3 this always produces a float which will cause problems for ncos if selfnmax/rotsym is bigger than dofmax.

S4.2 Original scans used for the Goebench challenge

Here comes a technical description on what was done to the files obtained from Gaussian scans.

The originally submitted scans for the Goebench challenge [6] already contained some manual editing. We discuss these for the scans but use TAMkinTools throughout this study to obtain the corresponding manipulations.

S4.2.1 Methanol - furan dimer

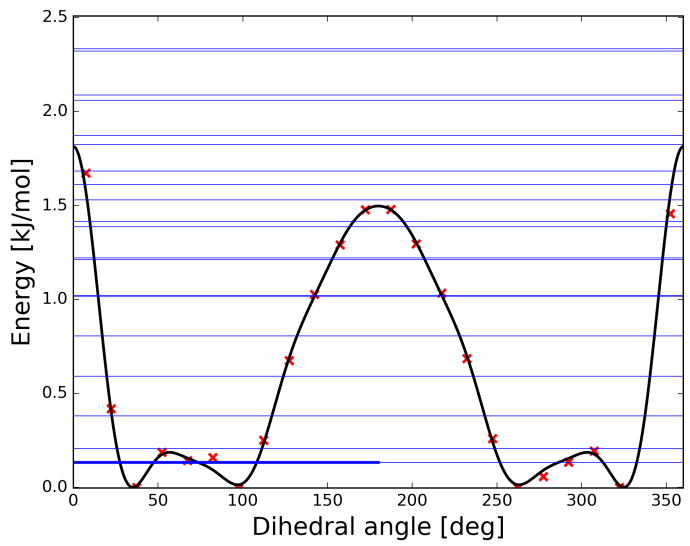

Figure S30: Methanol – furan OH scan treated like TAMkin rotors as submitted to the Goebench challenge [6, 7]. The scan was performed along the C–O–O–C dihedral involving the furan oxygen and an adjacent carbon as well as the methanol oxygen and carbon.

OH-bonded configuration:

```
OHb    = load_molecule_g03fchk("OHbfreq.fchk")
scanOH = load_rotscan_g03log("OHb_scan1n_repl.log")
rotor  = Rotor(scanOH, OHb, rotsym=1, cancel_freq='scan', even=True, dofmax=9, num_levels=level_prec)
```

The OHb_scan1n has 24 points with -15 degrees. It starts in the "top" configuration, switches to "plane" and rotates back to "top". The scan is used as is, but point 24 did not converge ("– Number of steps exceeded" instead of " – Stationary point found") and the last point (number 25) was removed (" - Stationary point found") because it seems stuck in the "plane" configuration but has the same dihedral angle value as the minimum and would confuse Tamkin.

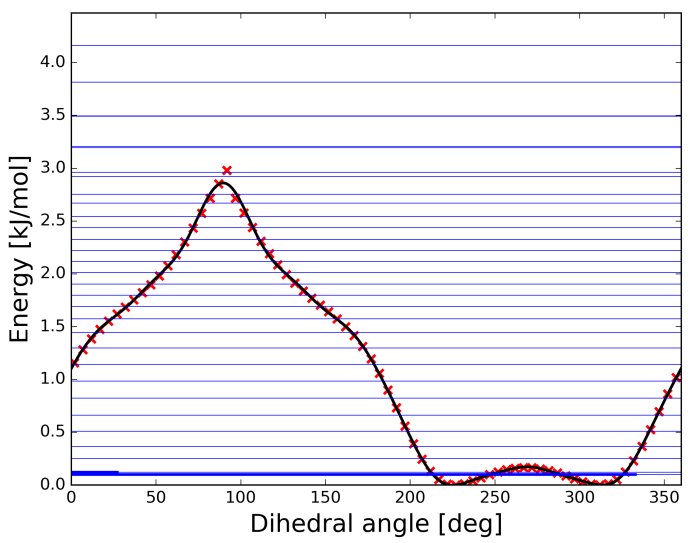

Figure S31: Methanol-furan π scan treated like TAMkin rotors as submitted to the Goebench challenge [6, 7]. The scan was performed along the C–C–O–C angle involving the two furan carbons opposite to the oxygen and the methanol oxygen and carbon (for π-bonded dimers, choosing a descriptive dihedral angle for the rotations was ambigous since the methanol is π-stacked to the furan plane and one might choose any two reference atoms of the furan ring).

π-bonded configuration:

```
PI     = load_molecule_g03fchk("PIfreq.fchk")
scanPI = load_rotscan_g03log("PI_torsp_repl.log")
rotor  = Rotor(scanPI, PI, rotsym=1, cancel_freq='scan', even=False, dofmax=10, num_levels=level_prec)
```

The scan "PI_torsp.log" was used as is. It contains 72 points (5 degrees distance). No changes were necessary. The scan shows a little jump at the maximum of the potential energy surface (PES) due to coupling

S4.2.2 Methanol – 2-methylfuran dimer

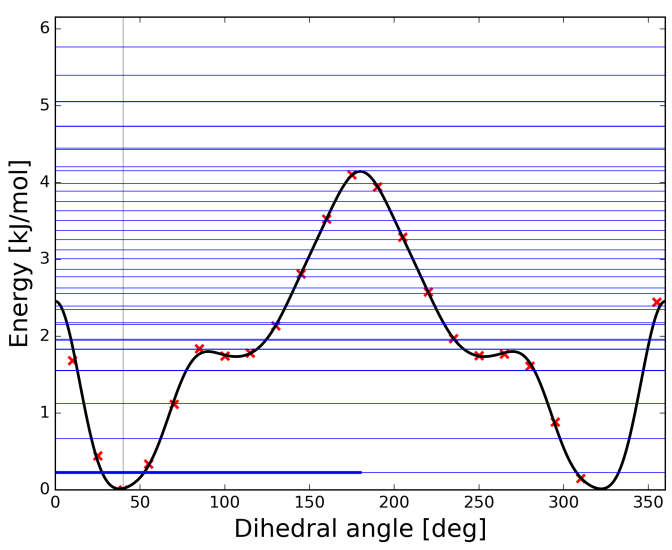

Figure S32: Methanol – 2-methylfuran OH scan close to those of Goebench challenge [6, 7]; for description cf. S30.

OH-bonded configuration:

```
OHa            = load_molecule_g03fchk("OHafreq.fchk")
OHb            = load_molecule_g03fchk("OHbfreq.fchk")
scanOH         = load_rotscan_g03log("scan_OHb_n_repl.log")
rotor          = Rotor(scanOH, OHb, rotsym=1, cancel_freq='scan', even=True, dofmax=10, num_levels=level_prec)
```

This scan starts in "top" configuration Ot and contains 24 steps of 15 degrees. Only the scan in negative direction "scan_OHb_n.log" was used where we erased points 4 to 6. The hindered rotor profile shows mirror symmetry, but, due to coupling, on the way from the lowest-energy Ot conformation to its mirror image, the energy raises further up and suddenly drops to the lowest-energy conformation mirror image, cf. Fig. S32. Therefore, three points were discarded and even symmetry was imposed on the fit.

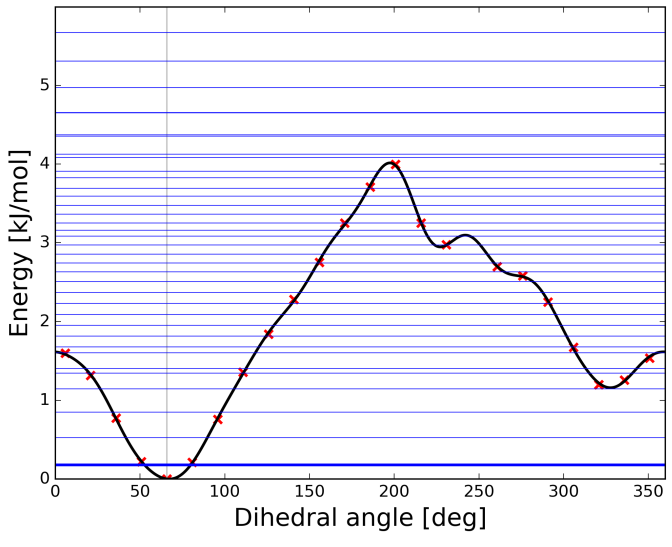

Figure S33: Methanol – 2-methylfuran π scan close to those of Goebench challenge [6, 7]; for description cf. S31.

π-bonded configuration: For this unsymmetric partner 2-methylfuran, two π-bonded conformations exist. In one (PIa), the methanol oxygen is close to the branch carbon (with that our scan starts), in the other, it is most distant from it.

```
PIa             = load_molecule_g03fchk("PIafreq.fchk")
PIb             = load_molecule_g03fchk("PIbfreq.fchk")
scanPI          = load_rotscan_g03log("scan_PIa_p_repl.log")
rotor           = Rotor(scanPI, PIa, rotsym=1, cancel_freq='scan', even=False, dofmax=10, num_levels=level_prec)
```

The scan is based on PIa. It has been used as is, but one point (scan point 13 of the original scan) is completely deleted.

S4.2.3 Methanol - 2,5-dimethylfuran dimer

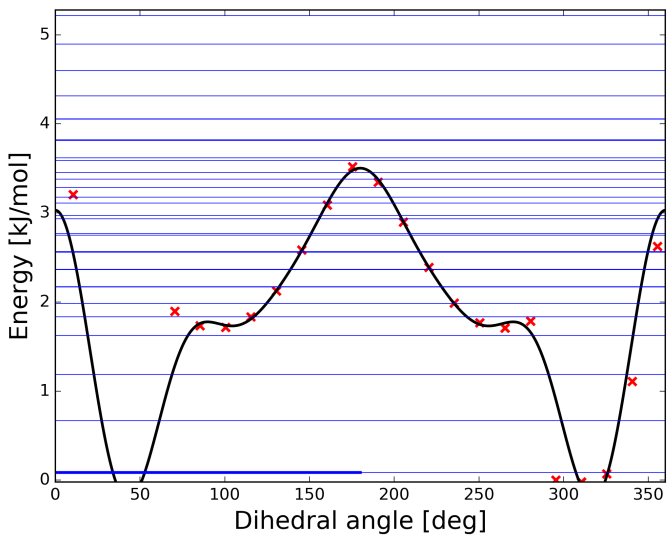

Figure S34: Methanol – 2,5-dimethylfuran OH scan close to those of Goebench challenge [6, 7]; for description cf. S30. The discontinuity near 280° causes the fit to undershoot the minimum.

OH-bonded structure:

```
OHa             = load_molecule_g03fchk("OHa.fchk")
OHb             = load_molecule_g03fchk("OHb.fchk")

scanOH          = load_rotscan_g03log("OHa_repl.log")

rotor           = Rotor(scanOH, OHb, rotsym=1, #cancel_freq='scan',
 even=True, dofmax=7, num_levels=level_prec)
```

The OH-bonded methanol - 2,5-dimethylfuran dimer scan shows several discontinuities. The total scan profile is therefore combined from two scans in opposite directions[4]. The discontinuity (the steep jump) near the global minimum leads to undershooting of the fit below the zero of energy and a shift of the minimum, cf. Fig. S34. To partly remedy this, Originally, point 4 is repeated seven times to emphasize it; in this study we use the weights array instead, but the fit using 7 functions still does not satisfactorily reproduce the global minimum. The last scan points of OHa++ are discarded because they overlap with the scan in the opposite direction, but at higher energy.

[4] 9 points in positive and 15 points in negative direction. In the overlap region, the points with higher energy were removed (from the positive-direction scan)

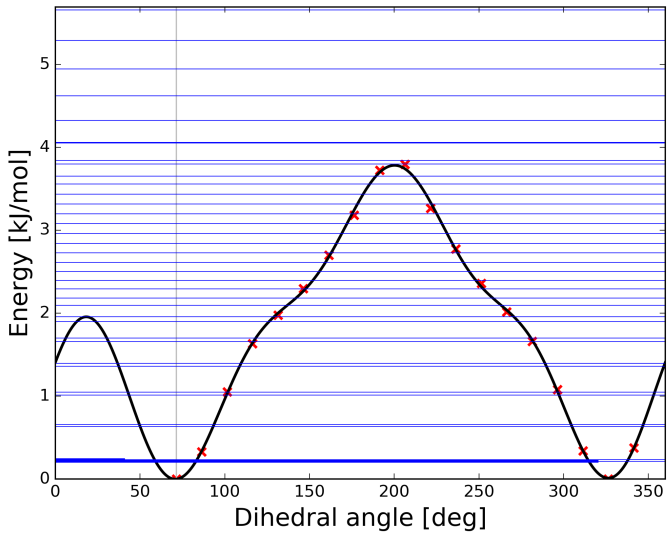

Figure S35: Methanol – 2,5-dimethylfuran π scan close to those of Goebench challenge [6, 7]; for description cf. S31.

π-bonded configuration:

```
PI     = load_molecule_g03fchk("PIfreq.fchk")
scanPI = load_rotscan_g03log("scan_PI_p_repl.log")
rotor  = Rotor(scanPI, PI, rotsym=1, cancel_freq='scan', even=False, dofmax=5, num_levels=level_prec)
```

The scan was taken in positive direction for 24 steps of 15 degrees. For the π-bonded configuration of the methanol – 2,5-dimethylfuran dimer the continuous scan from Gaussian was satisfactorily fitted by 5 Fourier functions, cf. Fig S35[5].

S4.3 Improved Scans

S4.3.1 Methanol – furan dimer

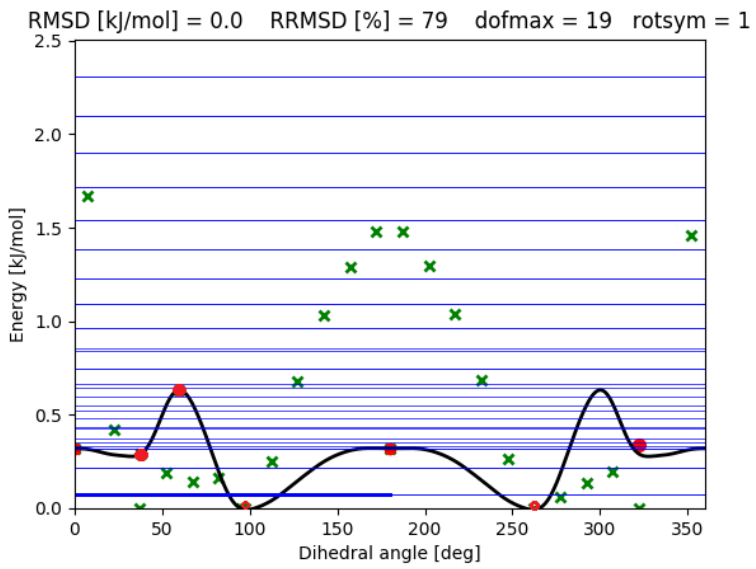

Figure S36: Methanol – furan OH scan improved by the TAMkinTools functions from this study. The scan points are the same as in Fig. S30 and the scan was performed along the C–O–O–C dihedral involving the furan oxygen and an adjacent carbon as well as the methanol oxygen and carbon.

OH bonded configuration

```
OHa            = load_molecule_g03fchk("OHafreq.fchk",energy = -345.35949810)
OHb            = load_molecule_g03fchk("OHbfreq.fchk",energy = -345.35938693)

scanOH         = load_rotscan_g03log("OHb_scan1n_repl.log")
original_angle, original_energy = scanOH.potential
scanOH_erased = erase_point_scan(scanOH,23)

scanOH_added_tshigh = add_point(scanOH_erased,        180.0*numpy.pi/180.0, 0.321615812/2625.4995+ref_energy) #TShigh
scanOH_hi2          = add_point(scanOH_added_tshigh,    0.0*numpy.pi/180.0, 0.321615812/2625.4995+ref_energy) #TShi-0
scanOH_low          = add_point(scanOH_hi2,          59.25*numpy.pi/180.0, 0.633926854/2625.4995+ref_energy) #TSlow
scanOH_ref1         = add_point(scanOH_low,          37.69*numpy.pi/180.0, 0.292/2625.4995+ref_energy)#first ref energy
scanOH_complete     = add_point(scanOH_ref1,         95.11*numpy.pi/180.0, 0.0/2625.4995+ref_energy)#second ref energy
angles,energies     = scanOH_complete.potential

myderivateposition  = [180.0*numpy.pi/180.0,
                          0.0*numpy.pi/180.0,
                       59.25*numpy.pi/180.0,
                       37.69*numpy.pi/180.0,
                       95.11*numpy.pi/180.0]

thetas = np.asarray([0.0,59.25,180.0,360.0-59.25])/360.0*2.0*numpy.pi
```

[5]Only one point (no. 20) was discarded because it had issues with forming derivatives of the scf energy and the optimization aborted.

```
rotor          = Opt_Rotor(scanOH_complete, OHb, rotsym=1, cancel_freq='scan', weights =myweights,
                           derivatives = myderivative, even=True, dofmax=14, num_levels=level_prec)
```

Inclusion of DLPNO-coupled-cluster singles, doubles, and perturbative triples (CCSD(T))/aug-cc-pv(t,q)z SPE makes the Op configuration the global minimum, cf. Fig. S37. Zero-point energy (ZPE) is also slightly lowered, mostly because the energies of the highest-energy TSs at DFT level become considerably lower at CCSD(T) level. The coupled-cluster energies can influence in principle even the frequencies (that correspond to the hindered rotation mode) at the minima *via* the corresponding change in curvature, though clearly more high-level points would be necessary to accurately reproduce coupled-cluster (CC) frequencies.

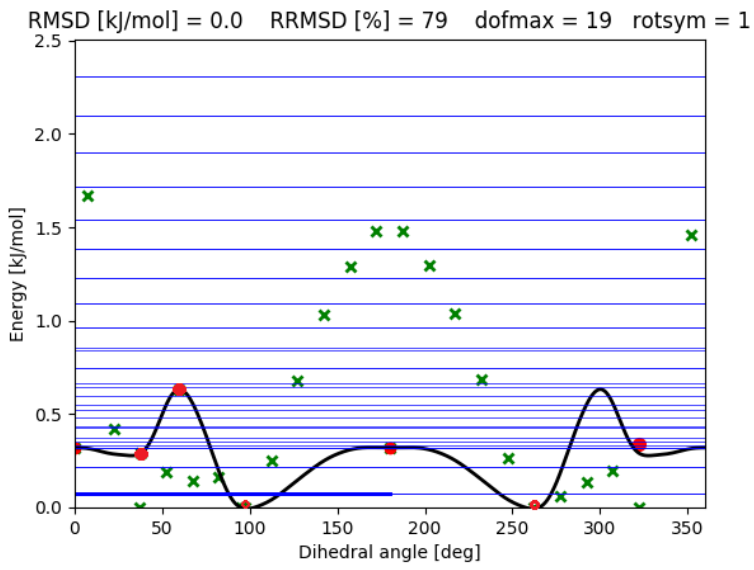

Figure S37: Methanol – furan OH scan improved by the TAMkinTools functions from this study. The scan points are the same as in Fig. S30 and the scan was performed along the C–O–O–C dihedral involving the furan oxygen and an adjacent carbon as well as the methanol oxygen and carbon.

OH bonded configuration - 5z

```
OHa            = load_molecule_g03fchk("OHa_flip_freq.fchk",energy = -345.33313601)
OHb            = load_molecule_g03fchk("OHbfreq.fchk",energy = -345.33313809)

scanOH_added_tshigh = add_point(scanOH_erased,        180.0*numpy.pi/180.0, 0.344137/2625.4995+ref_energy) #TShigh
scanOH_hi2          = add_point(scanOH_added_tshigh,    0.0*numpy.pi/180.0, 0.344137/2625.4995+ref_energy) #TShi-0
scanOH_low          = add_point(scanOH_hi2,           59.25*numpy.pi/180.0, 0.372661/2625.4995+ref_energy) #TSlow
scanOH_ref1         = add_point(scanOH_low,           37.69*numpy.pi/180.0, 0.00/2625.4995+ref_energy)#first ref energy
scanOH_complete     = add_point(scanOH_ref1,          95.11*numpy.pi/180.0, 0.005445/2625.4995+ref_energy)#second ref energy
angles,energies     = scanOH_complete.potential

rotor          = Opt_Rotor(scanOH_complete, OHb, rotsym=1, cancel_freq='scan', weights =myweights,
                           derivatives = myderivative, even=True, dofmax=14, num_levels=level_prec)
```

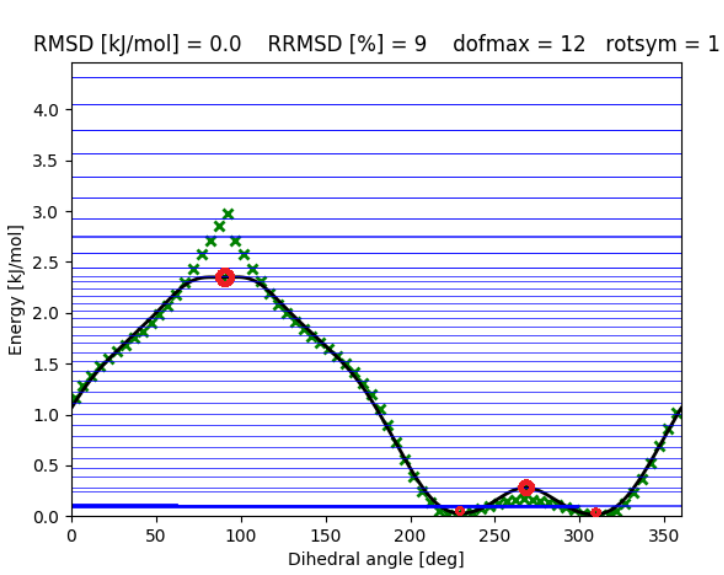

Figure S38: Methanol – furan π scan improved by the TAMkinTools functions from this study. The scan points are the same as in Fig. S31.

PI bonded configuration

```
scanPI0        = add_point(scanPI, -135.75453*numpy.pi/180.0, 0.00/2625.4995+ref_energy) # Min_mirror
scanPI1        = add_point(scanPI0, -48.17849*numpy.pi/180.0, 0.00/2625.4995+ref_energy) # Min
scanPI2        = add_point(scanPI1,  89.49808*numpy.pi/180.0, 2.35/2625.4995+ref_energy) # TShi
scanPI3        = add_point(scanPI2, -91.96651*numpy.pi/180.0, 0.28/2625.4995+ref_energy) # TSlo

myderivativevalues  = [0.0 for i in range(4)]
myderivateposition  = [-135.75453*numpy.pi/180.0,
                       -48.17849*numpy.pi/180.0,
```

```
                        89.49808*numpy.pi/180.0,
                       -91.96651*numpy.pi/180.0]

myderivateweights = [0.1 for i in range(4)]
myderivative = [myderivativevalues,myderivateposition,myderivateweights]

rotor          = Opt_Rotor(scanPI3, PI, rotsym=1, cancel_freq='scan', weights=myweights,
                           derivatives = myderivative,
                           even=False, dofmax=14, num_levels=level_prec)
```

For this dimer, inclusion of optimized stationary points and their updated SPEs hardly changes the results, cf. Fig. S38. The added stationary points are given higher weight (100) while to the original points is given relatively lower weight (0.1) so that the minimization of curvature leads to a smooth behavior near the added high-level points.

S4.3.2 Methanol – 2-methylfuran dimer

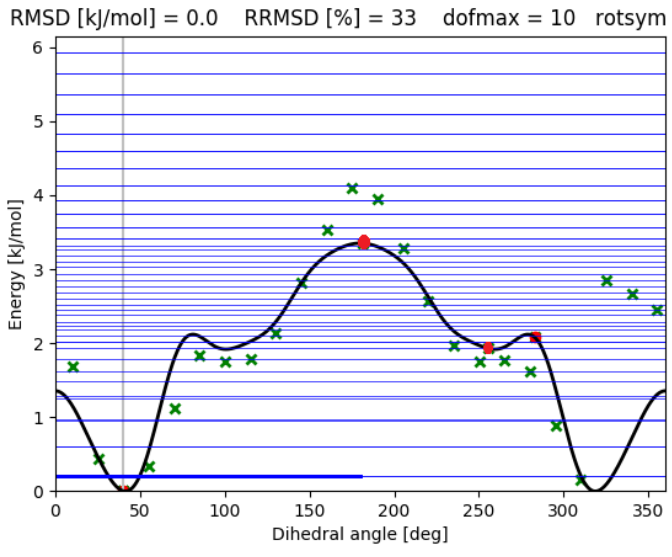

Figure S39: Methanol – 2-methylfuran OH scan improved by the TAMkinTools functions from this study. The scan points are the same as in Fig. S30 and the scan was performed along the C–O–O–C dihedral involving the furan oxygen and an adjacent carbon as well as the methanol oxygen and carbon.

OH bonded configuration

```
OHa            = load_molecule_g03fchk("OHafreq.fchk", energy=-384.62550256)
OHb            = load_molecule_g03fchk("OHbfreq.fchk", energy=-384.62623701)

scanOH         = load_rotscan_g03log("scan_OHb_n_repl.log")

scanOH_ref    = add_point(scanOH,       40.04135*numpy.pi/180.0, 0.00/2625.4995+ref_energy) #Ot
scanOH_low    = add_point(scanOH_ref,  -77.19415*numpy.pi/180.0, 2.08/2625.4995+ref_energy) #TSlow
scan_OHhigh   = add_point(scanOH_low,  -178.4621*numpy.pi/180.0, 3.35/2625.4995+ref_energy) #TShigh
scan_OHconf2  = add_point(scan_OHhigh, -104.8774*numpy.pi/180.0, 1.93/2625.4995+ref_energy) #Op

myweights = [0.1 for i in range(25)]
myweights[4] = 0.0
myweights[5] = 0.0
myadded_points = [[  40.04135*numpy.pi/180.0,
                    -77.19415*numpy.pi/180.0,
                   -178.4621*numpy.pi/180.0,
                   -104.8774*numpy.pi/180.0],
                  [0.00/2625.4995+ref_energy,
                   2.08/2625.4995+ref_energy,
                   3.35/2625.4995+ref_energy,
                   1.93/2625.4995+ref_energy]]

rotor          = Opt_Rotor(scan_OHconf2, OHb, rotsym=1, cancel_freq='scan', even=True, weights = myweights,
                           derivatives = myderivatives, dofmax=14, num_levels=level_prec)
```

Introducing high-level CCSD(T) SPEs slightly raises the TS between the two minima, slightly increasing the curvature at the minima, cf. Fig. S39.

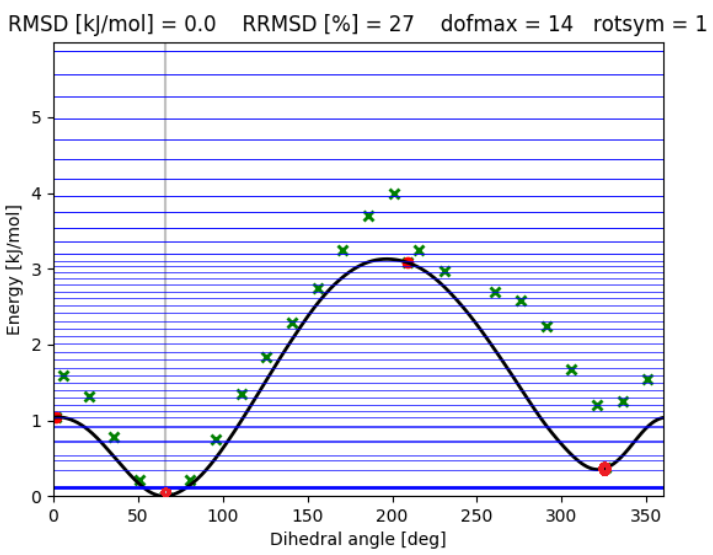

Figure S40: Methanol – 2-methylfuran π scan improved by the TAMkinTools functions from this study. The scan points are the same as in Fig. S31.

PI bonded configuration

```
PIa            = load_molecule_g03fchk("PIafreq.fchk", energy=-384.62546887)
PIb            = load_molecule_g03fchk("PIbfreq.fchk", energy=-384.62532931)

scanPI         = load_rotscan_g03log("scan_PIa_p_repl.log")
angles, energies = scanPI.potential
scanPI_corrected = erase_point_scan(scanPI,12)

nma_angle = dihed_angle(nma_PIa.coordinates[scanPI_corrected.dihedral])[0]

ref_energy = potential_reference(scanPI, nma_angle)

scan_PIhigh = add_point(scanPI_corrected, -150.69257/180.0*numpy.pi, 3.08/2625.4995+ref_energy) #TShigh
scan_PIlow  = add_point(scan_PIhigh,         1.20334/180.0*numpy.pi, 1.04/2625.4995+ref_energy) #TSlow
scan_PI2    = add_point(scan_PIlow,        -33.81733/180.0*numpy.pi, 0.37/2625.4995+ref_energy) #TSlow
scan_PI3    = add_point(scan_PI2,           65.75423/180.0*numpy.pi, 0.00/2625.4995+ref_energy) #TSlow

rotor          = Opt_Rotor(scan_PI3, PIa, rotsym=1, cancel_freq='scan', weights = myweights, derivatives=myderivative,
                           even=False, dofmax=14, num_levels=level_prec)
```

The optimized fit with TamkinTools avoids the artificial minimum by minimizing curvature, cf. Fig. S40.

S4.3.3 Methanol – 2,5-dimethylfuran dimer

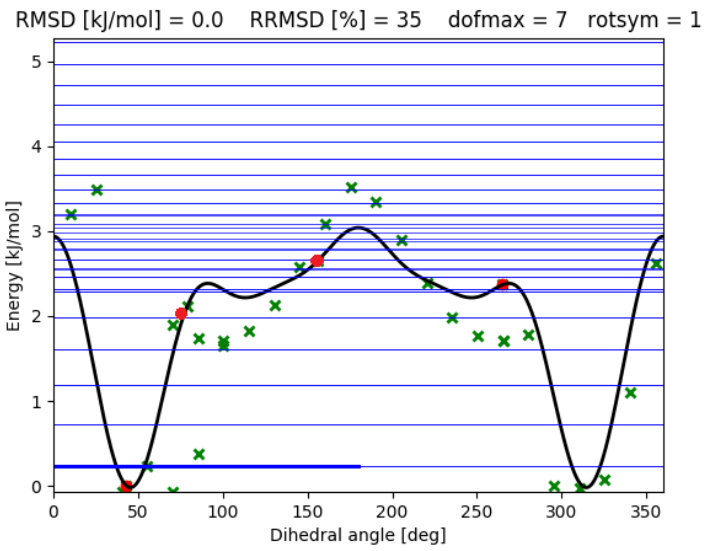

Figure S41: Methanol – 2,5-dimethylfuran OH scan improved by the TAMkinTools functions from this study. The scan points are the same as in Fig. S30 and the scan was performed along the C–O–O–C dihedral involving the furan oxygen and an adjacent carbon as well as the methanol oxygen and carbon.

OH bonded configuration

```
level_prec = 200
T_plot     = 1
ExtRotSym  = 1

OHa            = load_molecule_g03fchk("OHa.fchk", energy=-423.89133413)
OHb            = load_molecule_g03fchk("OHb.fchk", energy=-423.89223624)

scanOHpp         = load_rotscan_g03log("OHa++_repl.log")
scanOHn         = load_rotscan_g03log("OHa-_repl.log")
combscan = combine_Scan(scanOHn, scanOHpp)

scanmin0     = add_point(combscan,      43.16909*numpy.pi/180.0, 0.00/2625.4995+ref_energy) #Ot
scanmin1     = add_point(scanmin0,     -94.77078*numpy.pi/180.0, 2.37/2625.4995+ref_energy) #Op
scan_OHsmall = add_point(scanmin1,      79.10000*numpy.pi/180.0, 2.12/2625.4995+ref_energy) #TS
scan_OHfinal = add_point(scan_OHsmall, 156.00091*numpy.pi/180.0, 2.65/2625.4995+ref_energy) #TShigh
```

```
rotor          = Opt_Rotor(scan_OHfinal, OHb, rotsym=1, cancel_freq='scan',
                  even=True, weights = myweights, derivatives=myderivatives,
                  dofmax=14, num_levels=level_prec)
```

When corrected using TamkinTools, the PES matches the minima well, cf. Fig. S41. This also slightly increases the computed ZPE.

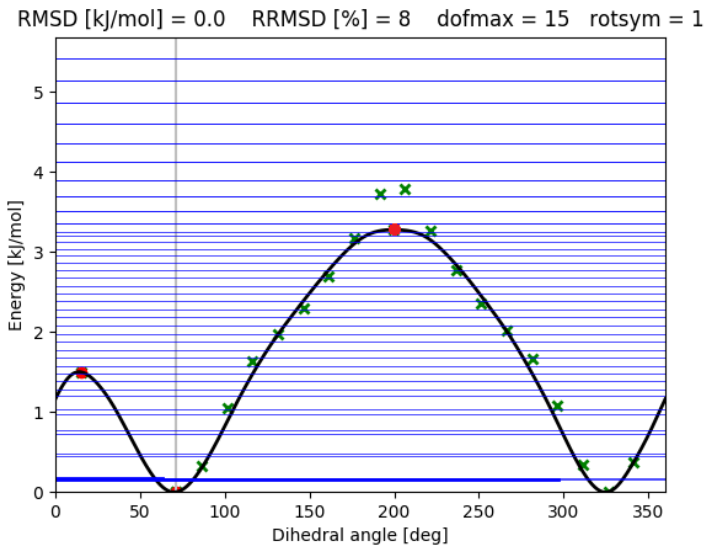

Figure S42: Methanol – 2,5-dimethylfuran π scan improved by the TAMkinTools functions from this study. The scan points are the same as in Fig. S31.

PI bonded configuration

```
PI             = load_molecule_g03fchk("PIfreq.fchk")

scanPI         = load_rotscan_g03log("scan_PI_p_repl.log")


scan_PI0    = add_point(scanPI,       71.3838*numpy.pi/180.0,(1.66-1.66)/2625.4995+ref_energy) #TSlow
scan_PIlow  = add_point(scan_PI0,     15.1597*numpy.pi/180.0,(3.16-1.66)/2625.4995+ref_energy) #TSlow
scan_PIhigh = add_point(scan_PIlow, -160.0900*numpy.pi/180.0,(4.94-1.66)/2625.4995+ref_energy) #TShigh

myweights = [0.1 for i in range(19)]

myweights[17] = 100 # also "stationary"

rotor          = Opt_Rotor(scan_PIhigh, rotsym=1, cancel_freq='scan', weights = myweights,
                           derivatives = myderivatives,
                           even=False, dofmax=14, num_levels=level_prec)
```

Optimized fits with TamkinTools that include DLPNO-CCSD(T) SPEs slightly lower the high-energy TS and enlarge the low-energy TS, cf. Fig S42; apart from that, the picture is unchanged.

S4.4 Zero-Point Energies

Vibrational ZPEs result already from rigid rotor harmonic oscillator (RRHO) treatments. In order to include the proper one-dimensional hindered rotor (1DHR) ZPE within the 'cancel_freq' treatment, a harmonic oscillator (HO) is fitted to the curvature and the total partition function is divided by this, that is the total ZPE is reduced by the ZPE of that HO. The partition function file will just print this ZPE. All in all, the total contribution of 1DHR treatment is the ZPE of the hindered rotor (HR) which is the corresponding energy level, minus the ZPE of the fitted HO.

For higher-energy conformations, TAMkin would still pertain to the lowest-energy minimum by producing negative energy levels. Instead, we take the first eigenvalue where the corresponding wave function shows a population peak in the well of the respective conformation as ZPE. For local minima, the energy of the eigenvalue is taken relative to the potential energy of the respective local minimum so that addition of the total ZPE to the respective potential energy yields the energy at 0 K

Table S30: ZPEs for all dimers in this study in kJ/mol; differences are given always with respect to the top Ot conformation. The first data column comprises pure unscaled RRHO ZPE corrections. The third represents the original TAMkin procedure involving the direct fit. The fifth comprises results from the optimized PES fitting procedure using TAMkinTools (this study). The PES for the HR treatment are based on CC aug-cc-pv(t,q)z extrapolation except for the values in parentheses that are based on aug-cc-pv5z energies.

Structure	RRHO	Δ_{Ot}	direct fit	Δ_{Ot}	opt. fit	Δ_{Ot}
Me-Fu Ot	322.77	0	322.71	0	322.95 (322.73)	0 (0)
Me-Fu Op	322.51	-0.26	322.61	-0.10	322.75 (322.48)	-0.20 (-0.25)
Me-Fu PI	321.94	-0.83	321.92	-0.78	321.92 (321.92)	-1.03 (-0.81)
Me-2mFu Ot	396.25	0	396.46	0	396.25	0
Me-2mFu Op	395.88	-0.37	395.91	-0.55	395.83	-0.41
Me-2mFu PIa	395.22	-1.03	395.22	-1.24	395.22	-1.03
Me-2mFu PIb	395.15	-1.10	395.17	-1.29	395.15	-1.09
Me-25dmFu Ot	469.12	0	469.06	0	469.16	0
Me-25dmFu Op	468.82	-0.31	468.67	-0.39	468.72	-0.44
Me-25dmFu PI	468.37	-0.75	468.31	-0.35	468.36	-0.33

S5 Selected probability density functions

All probability density functions plotted here contain some shift to make them better distinguishable from the axis.

S5.1 Original Goebench submission profiles

S5.1.1 Methanol – furan, OH-bonded

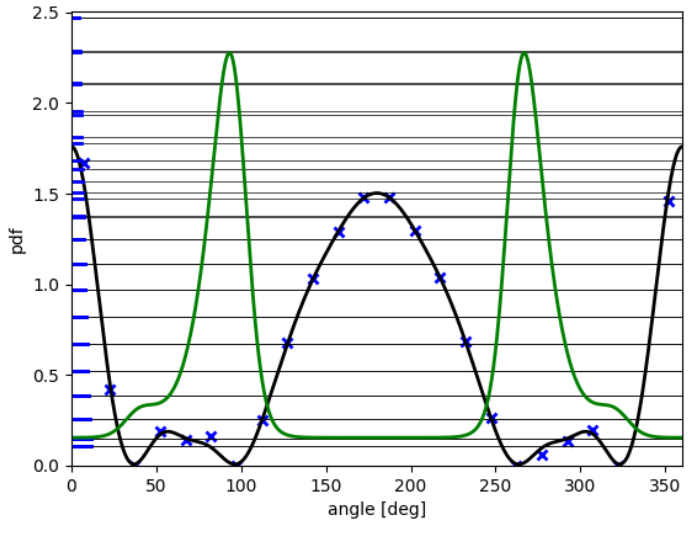

Figure S43: Probability density function for energy level 0.

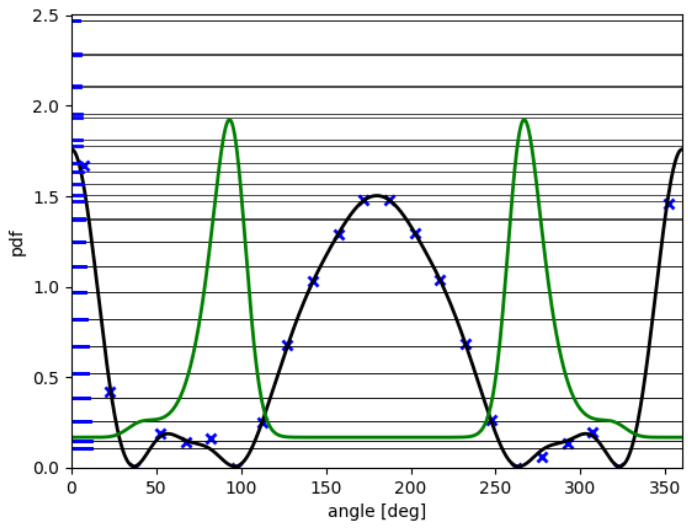

Figure S44: Probability density function for energy level 1.

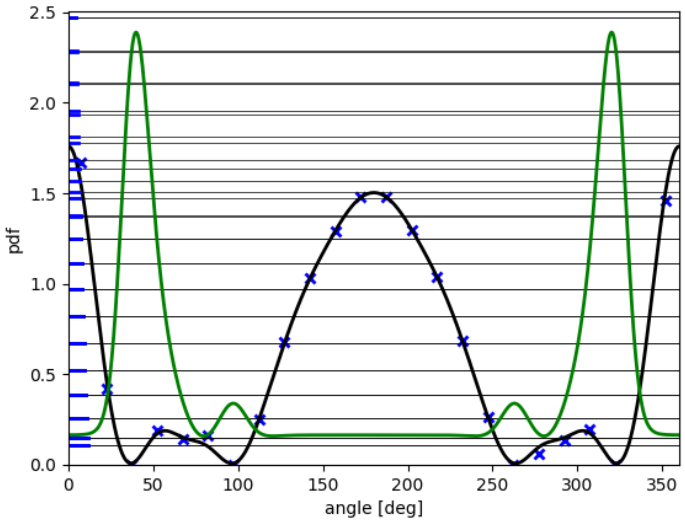

Figure S45: Probability density function for energy level 2.

S5.1.2 Methanol – 2-methylfuran

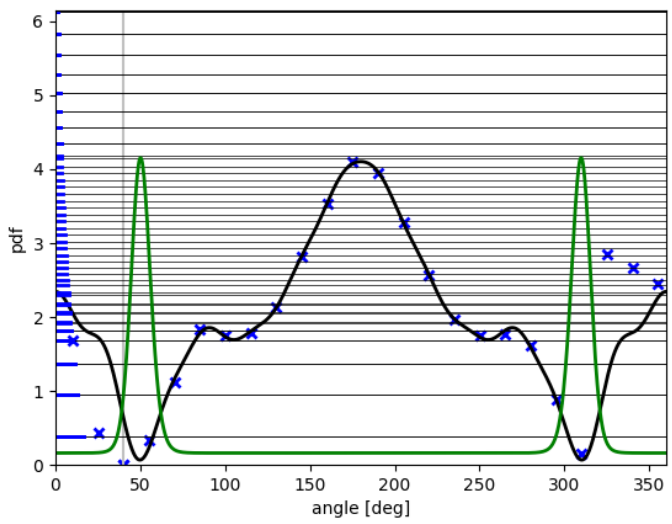

Figure S46: Probability density function for energy level 0.

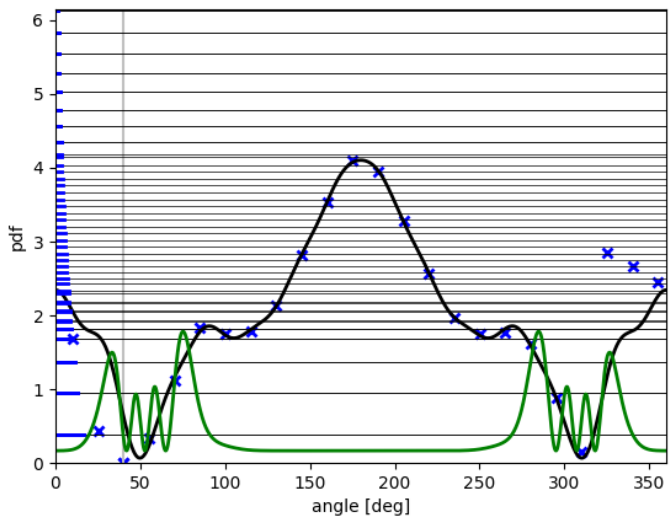

Figure S47: Probability density function for energy level 7.

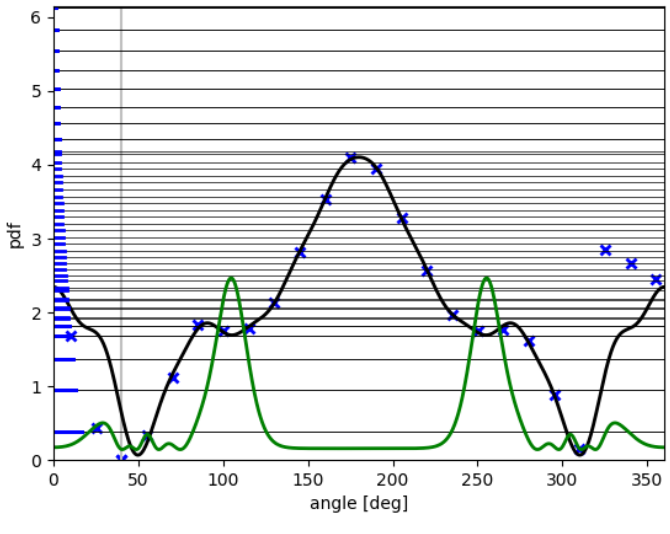

Figure S48: Probability density function for energy level 8.

OH-bonded conformation

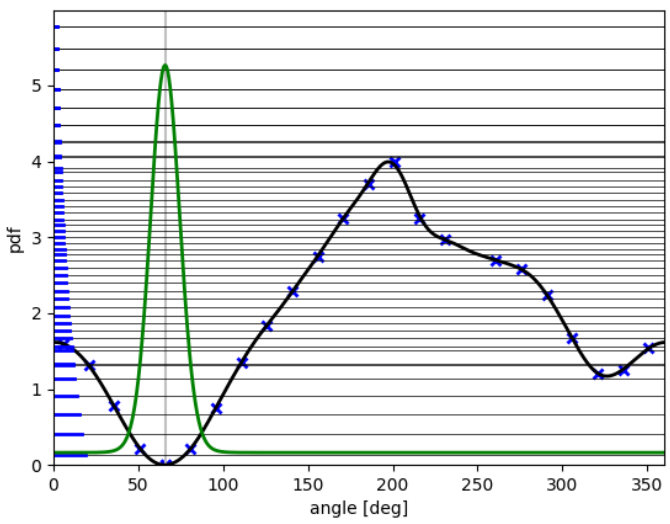

Figure S49: Probability density function for energy level 0.

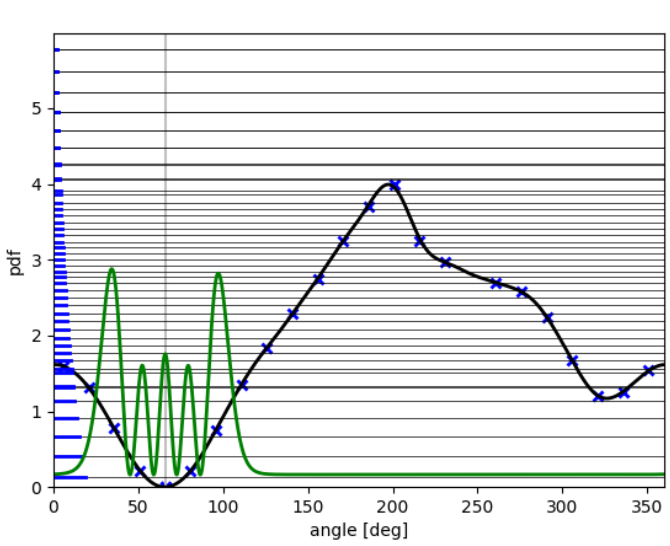

Figure S50: Probability density function for energy level 4.

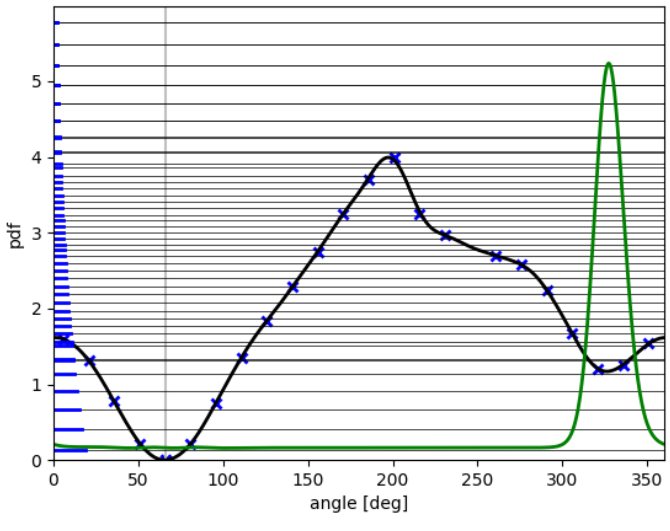

Figure S51: Probability density function for energy level 5.

PI-bonded conformation

S5.1.3 Methanol – 2,5-dimethylfuran, OH-bonded

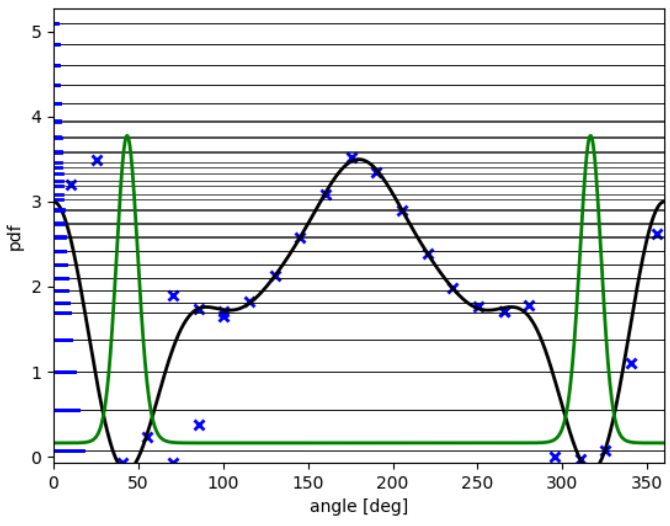

Figure S52: Probability density function for energy level 0.

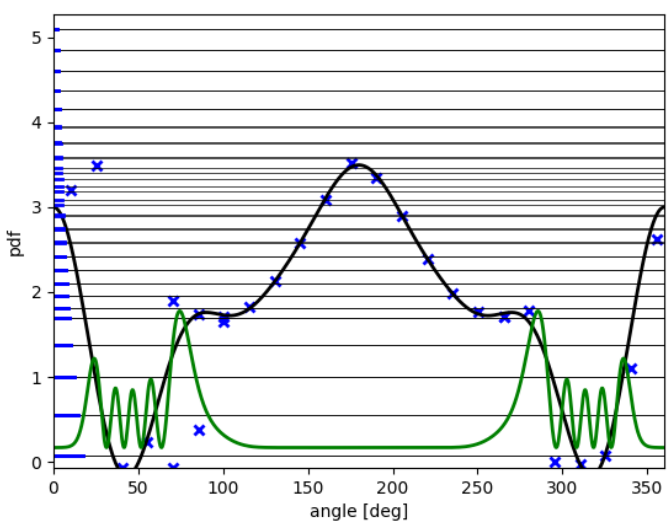

Figure S53: Probability density function for energy level 9.

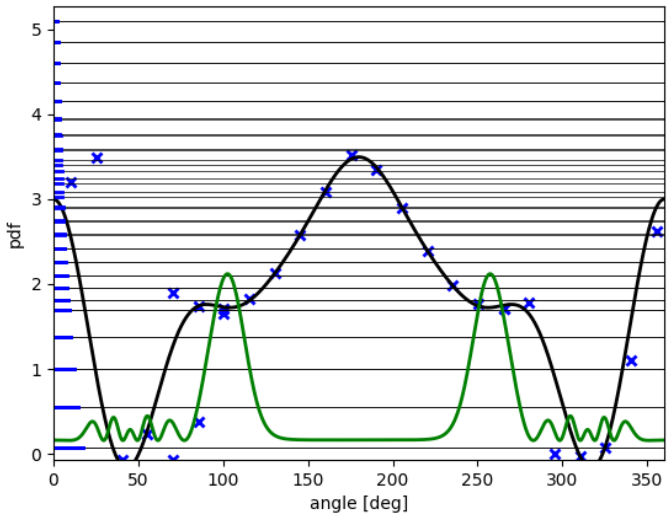

Figure S54: Probability density function for energy level 10.

S5.2 Improved profiles using TAMkinTools

S5.2.1 Methanol – furan, OH-bonded, aug-cc-pv5z

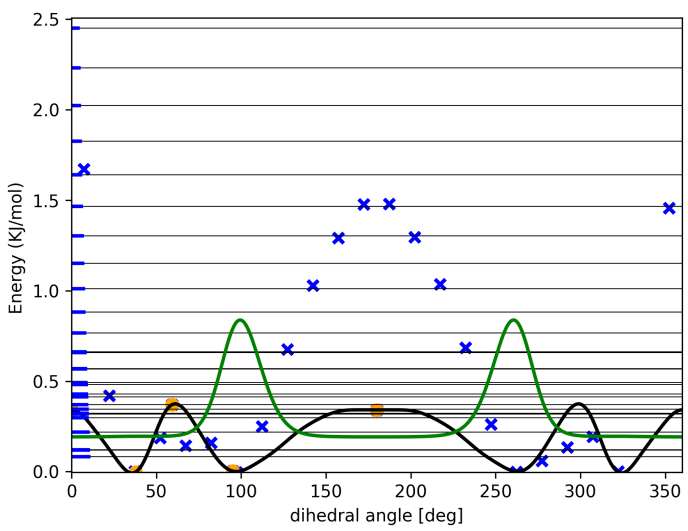

Figure S55: Probability density function for energy level 0.

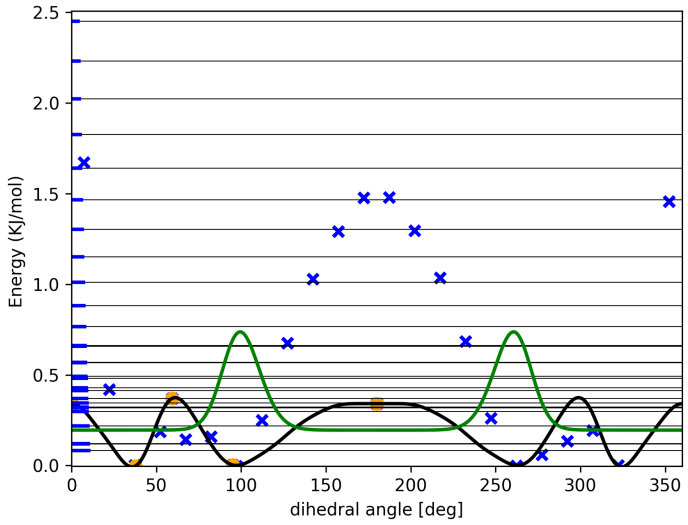

Figure S56: Probability density function for energy level 1.

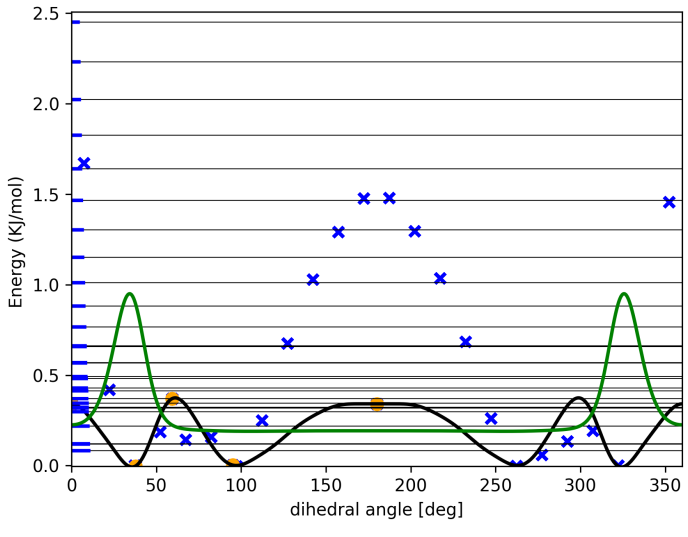

Figure S57: Probability density function for energy level 2.

S5.2.2 Methanol – furan, OH-bonded, aug-cc-pv(t,q)z

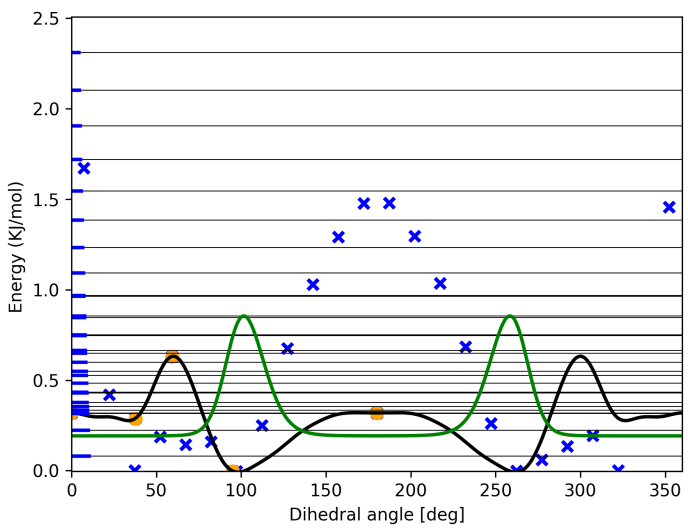

Figure S58: Probability density function for energy level 0.

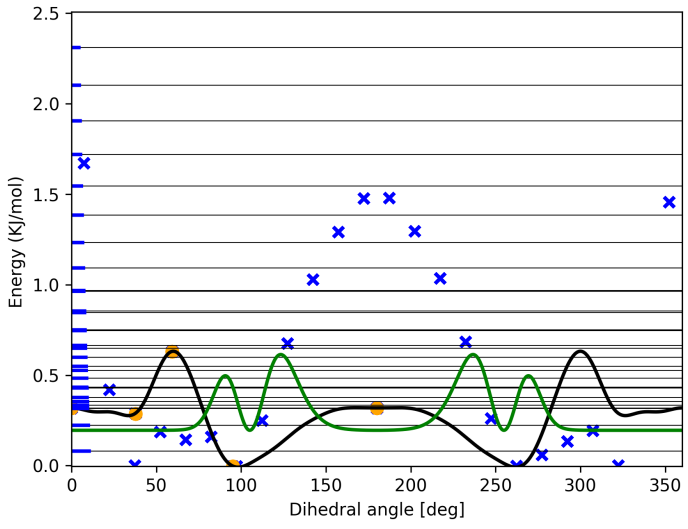

Figure S59: Probability density function for energy level 3.

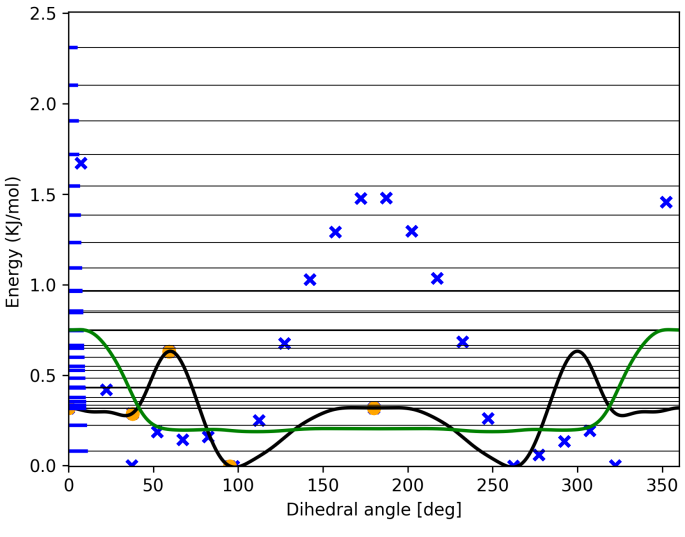

Figure S60: Probability density function for energy level 4.

S5.2.3 Methanol – 2-methylfuran

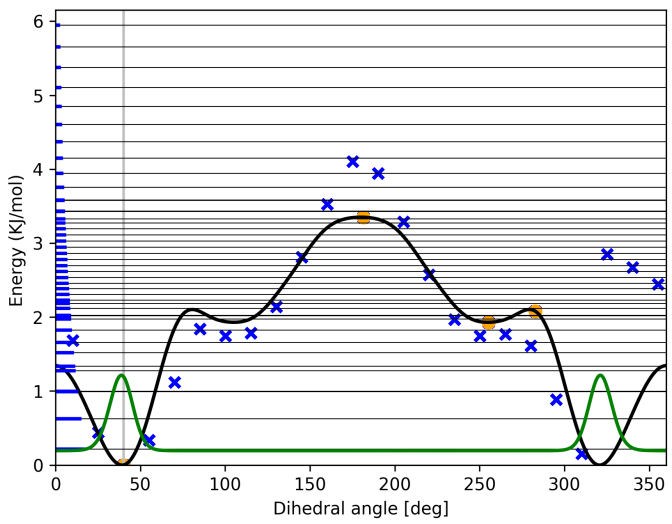

Figure S61: Probability density function for energy level 0.

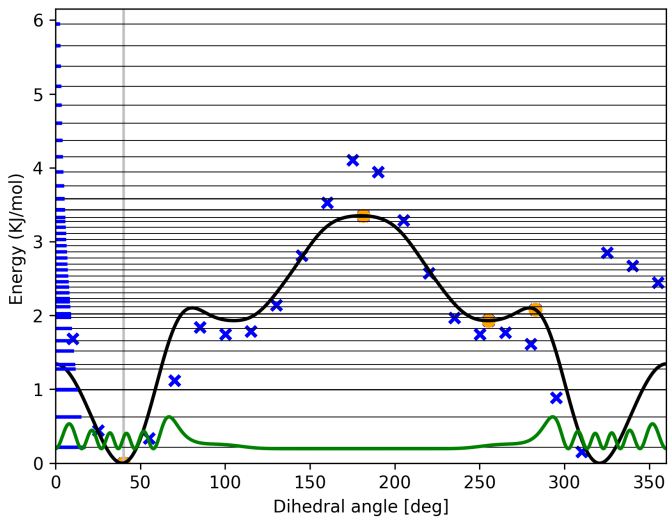

Figure S62: Probability density function for energy level 11.

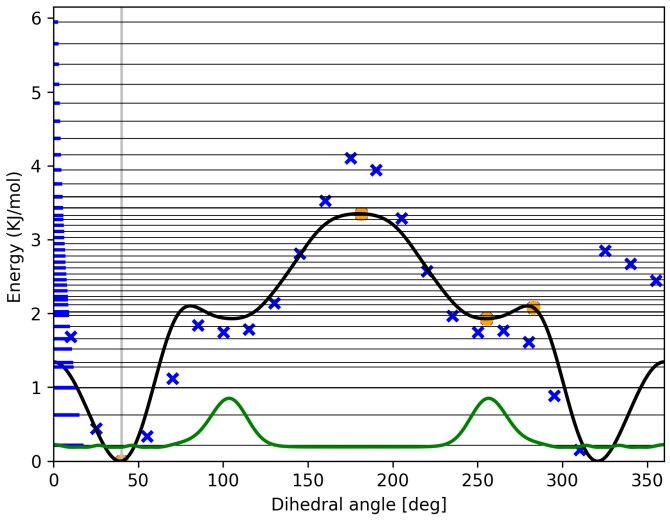

Figure S63: Probability density function for energy level 12.

OH-bonded conformation

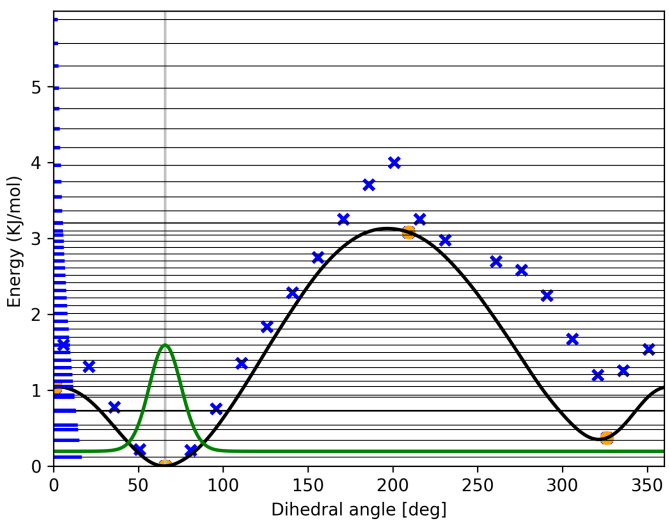

Figure S64: Probability density function for energy level 0.

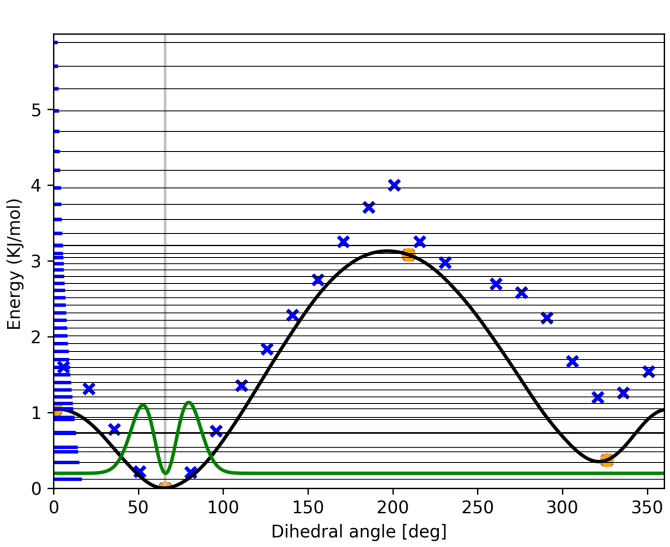

Figure S65: Probability density function for energy level 1.

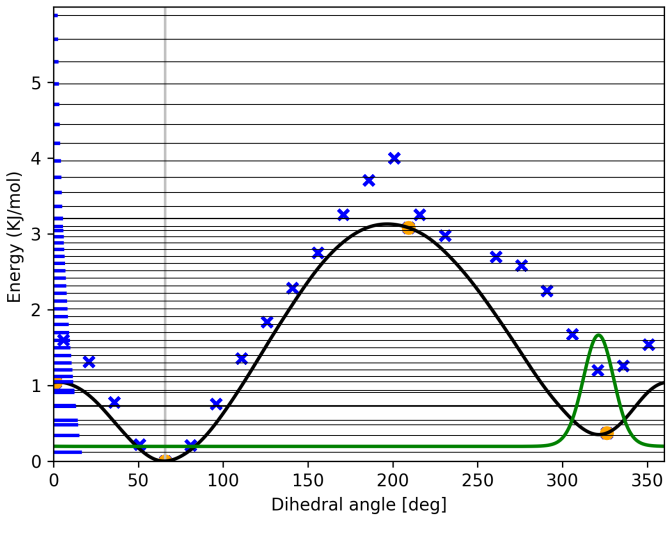

Figure S66: Probability density function for energy level 2.

PI-bonded conformation

S5.2.4 Methanol – 2,5-dimethylfuran, OH-bonded

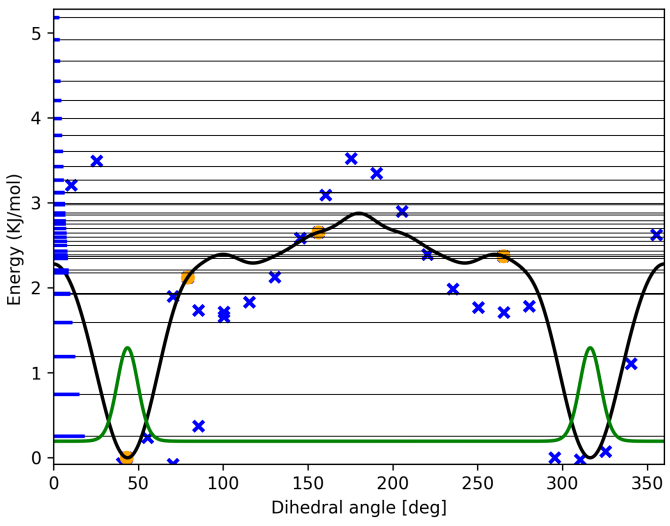

Figure S67: Probability density function for energy level 0.

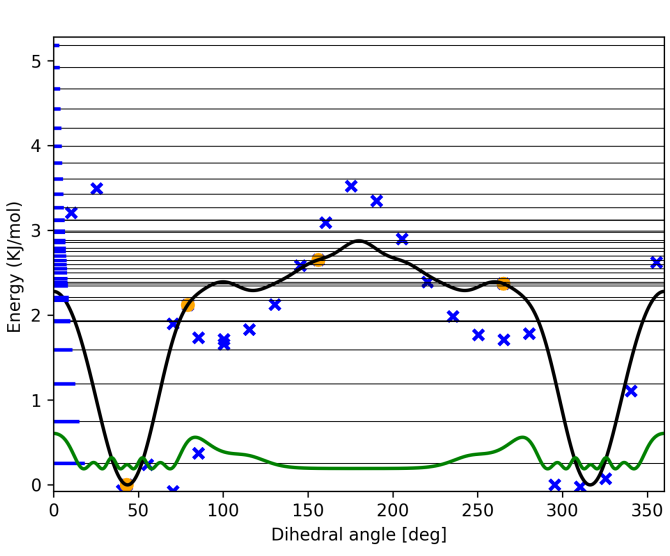

Figure S68: Probability density function for energy level 12.

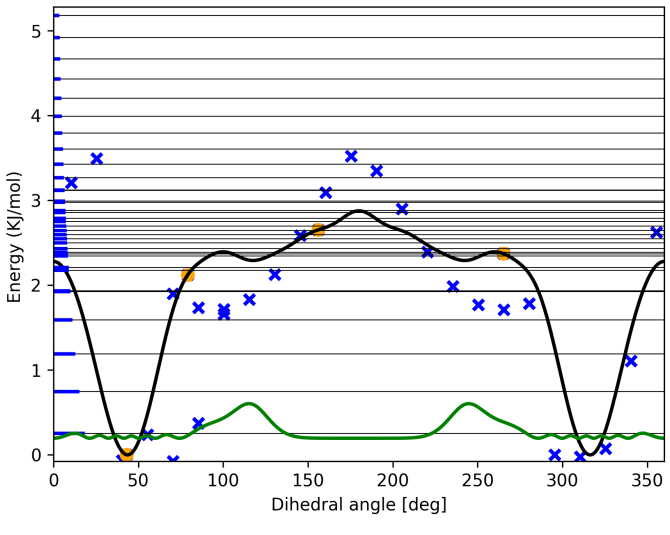

Figure S69: Probability density function for energy level 13.

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. Gaussian 09 Revision D.01, 2009. Gaussian Inc. Wallingford CT 2009.

[2] Frank Neese. The orca program system. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2(1):73–78, 2012.

[3] Frank Neese and Edward F. Valeev. Revisiting the atomic natural orbital approach for basis sets: Robust systematic basis sets for explicitly correlated and conventional correlated ab initio methods? *J. Chem. Theory Comput.*, 7(1):33–43, 2011. PMID: 26606216.

[4] Dimitrios G. Liakos, Manuel Sparta, Manoj K. Kesharwani, Jan M. L. Martin, and Frank Neese. Exploring the accuracy limits of local pair natural orbital coupled-cluster theory. *J. Chem. Theory Comput.*, 11(4):1525–1539, 2015.

[5] An Ghysels, Toon Verstraelen, Karen Hemelsoet, Michel Waroquier, and Veronique van Speybroeck. Tamkin: A versatile package for vibrational analysis and chemical kinetics. *Journal of Chemical Information and Modeling*, 50(9):1736–1750, 2010.

[6] Hannes C. Gottschalk, Anja Poblotzki, Martin A. Suhm, Muneerah M. Al-Mogren, Jens Antony, Alexander A. Auer, Leonardo Baptista, David M. Benoit, Giovanni Bistoni, Fabian Bohle, Rahma Dahmani, Dzmitry Firaha, Stefan Grimme, Andreas Hansen, Michael E. Harding, Majdi Hochlaf, Christof Holzer, Georg Jansen, Wim Klopper, Wassja A. Kopp, Leif C. Kröger, Kai Leonhard, Halima Mouhib, Frank Neese, Max N. Pereira, Inga S. Ulusoy, Axel Wuttke, and Ricardo A. Mata. The furan microsolvation blind challenge for quantum chemical methods: First steps. *J. Chem. Phys.*, 148(1):014301, 2018.

[7] Hannes C. Gottschalk, Anja Poblotzki, Mariyam Fatima, Daniel A. Obenchain, Cristóbal Pérez, Jens Antony, Alexander A. Auer, Leonardo Baptista, David M. Benoit, Giovanni Bistoni, Fabian Bohle, Rahma Dahmani, Dzmitry Firaha, Stefan Grimme, Andreas Hansen, Michael E. Harding, Majdi Hochlaf, Christof Holzer, Georg Jansen, Wim Klopper, Wassja A. Kopp, Małgorzata Krasowska, Leif C. Kröger, Kai Leonhard, Muneerah Mogren Al-Mogren, Halima Mouhib, Frank Neese, Max N. Pereira, Muthuramalingam Prakash, Inga S. Ulusoy, Ricardo A. Mata, Martin A. Suhm, and Melanie Schnell. The first microsolvation step for furans: New experiments and benchmarking strategies. *J. Chem. Phys.*, 152(16):164303, 2020.