Supporting Information for

Synthesis of a Tight Intramolecular OH---Olefin Interaction, Probed by IR, ^{1}H NMR and Quantum Chemistry

Mark D. Struble, Maxwell Gargiulo Holl, Gavin Coombs, Maxime A. Siegler, and

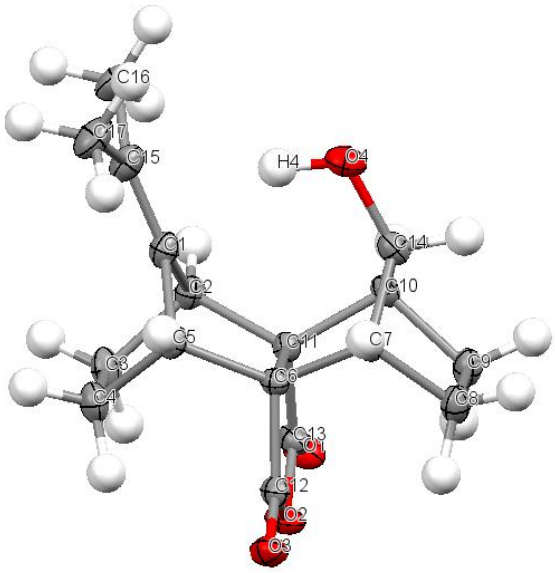
Thomas Lectka*

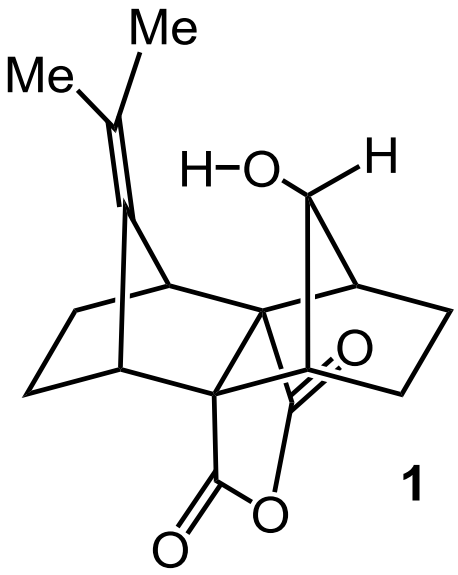
Contribution from the Department of Chemistry, New Chemistry Building, Johns

Hopkins University, 3400 North Charles Street, Baltimore, Maryland, 21218

lectka@jhu.edu

Table of Contents

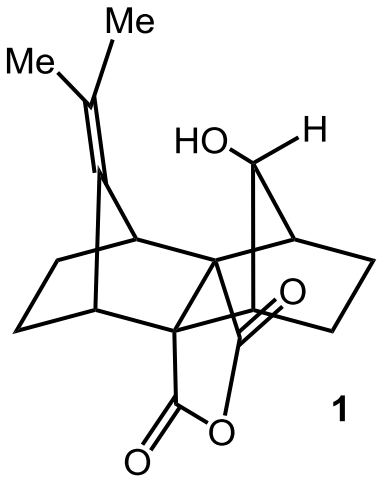




All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013) was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013 (Sheldrick, 2013) and was refined on F^2 with SHELXL-2013 (Sheldrick, 2013). Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 13, AFIX 23 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C atoms. The H atoms attached to O4 was found from difference Fourier map. The O4–H4 distance was restrained to 0.970(5) using the DFIX restraint, and refines to 0.963(7) Å.* The isotropic temperature factor was refined freely.

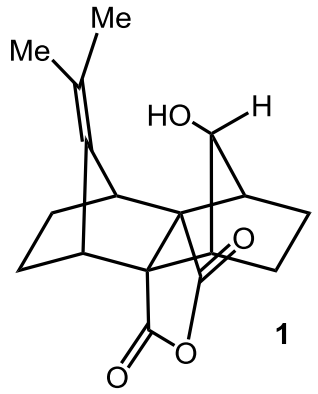
* This O–H bond distance was restrained so that both experimental and calculated values are consistent. The exact location of the H atom cannot be accurately determined via X-ray crystallography.

^{1}H spectrum of **1**



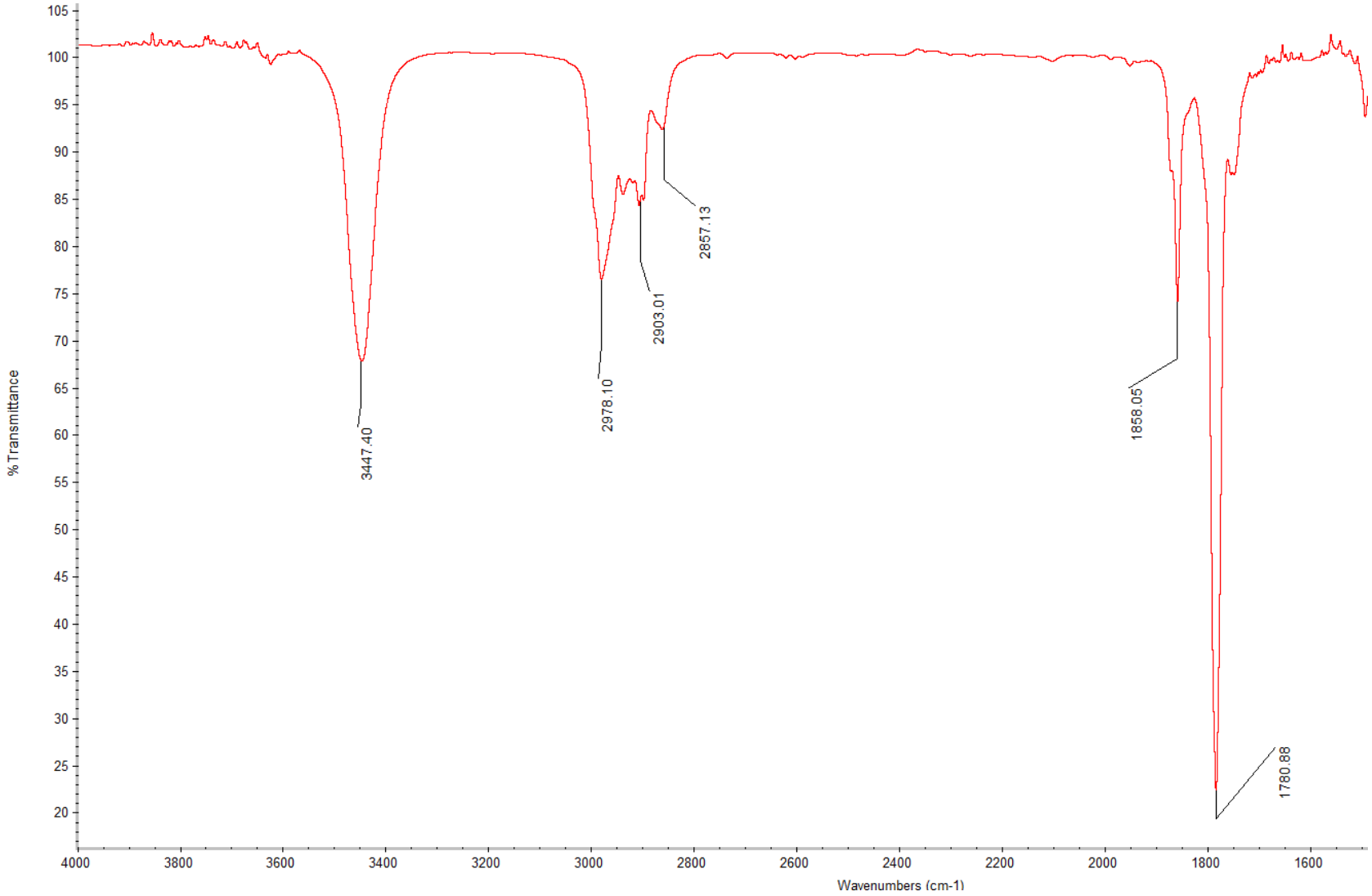
1

^{13}C spectrum of **1**

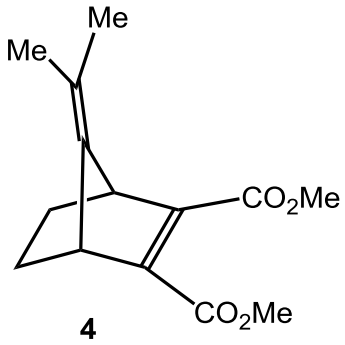


1

IR spectrum of **1** (CCl_4)

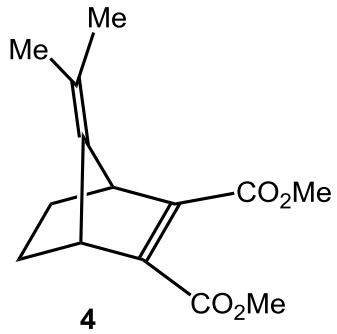


^{1}H spectrum of **4**



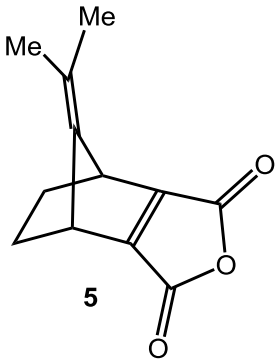
4

^{13}C spectrum of 4



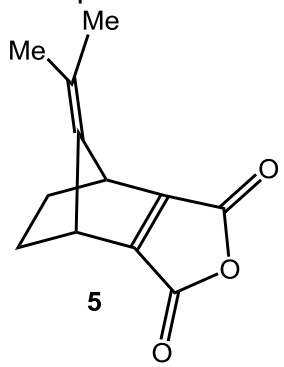
4

^{1}H spectrum of **5**



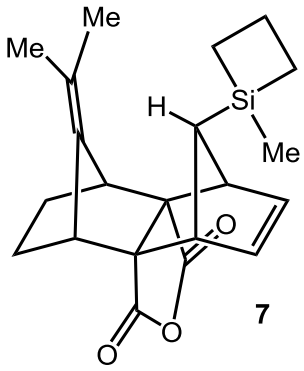
5

^{13}C spectrum of **5**



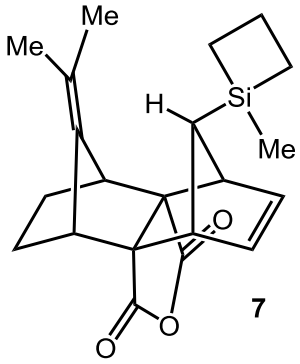
5

^{1}H spectrum of **7**



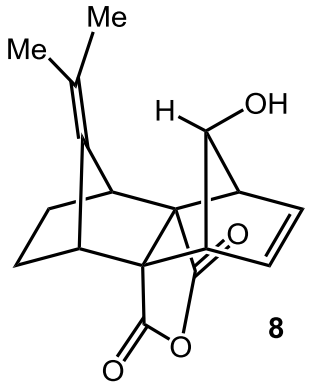
7

^{13}C spectrum of **7**



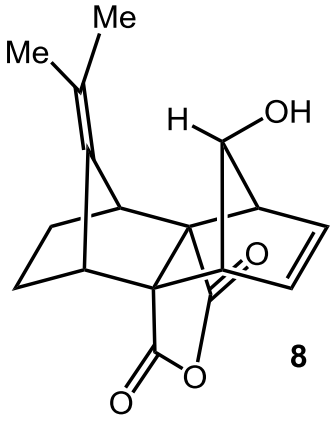
7

^{1}H spectrum of **8**



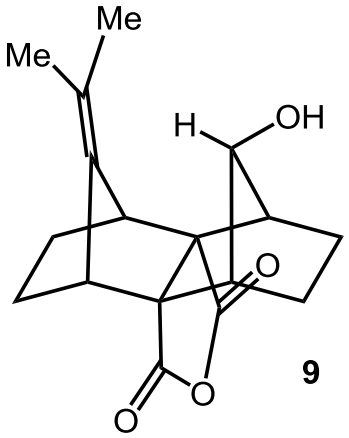
8

^{13}C spectrum of **8**



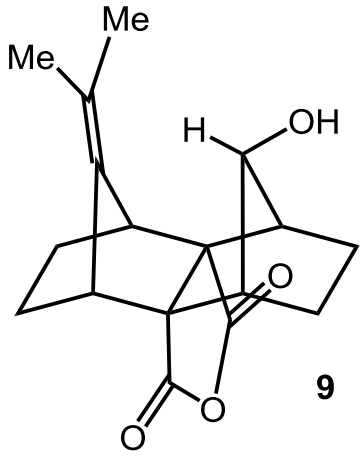
8

^{1}H spectrum of **9**



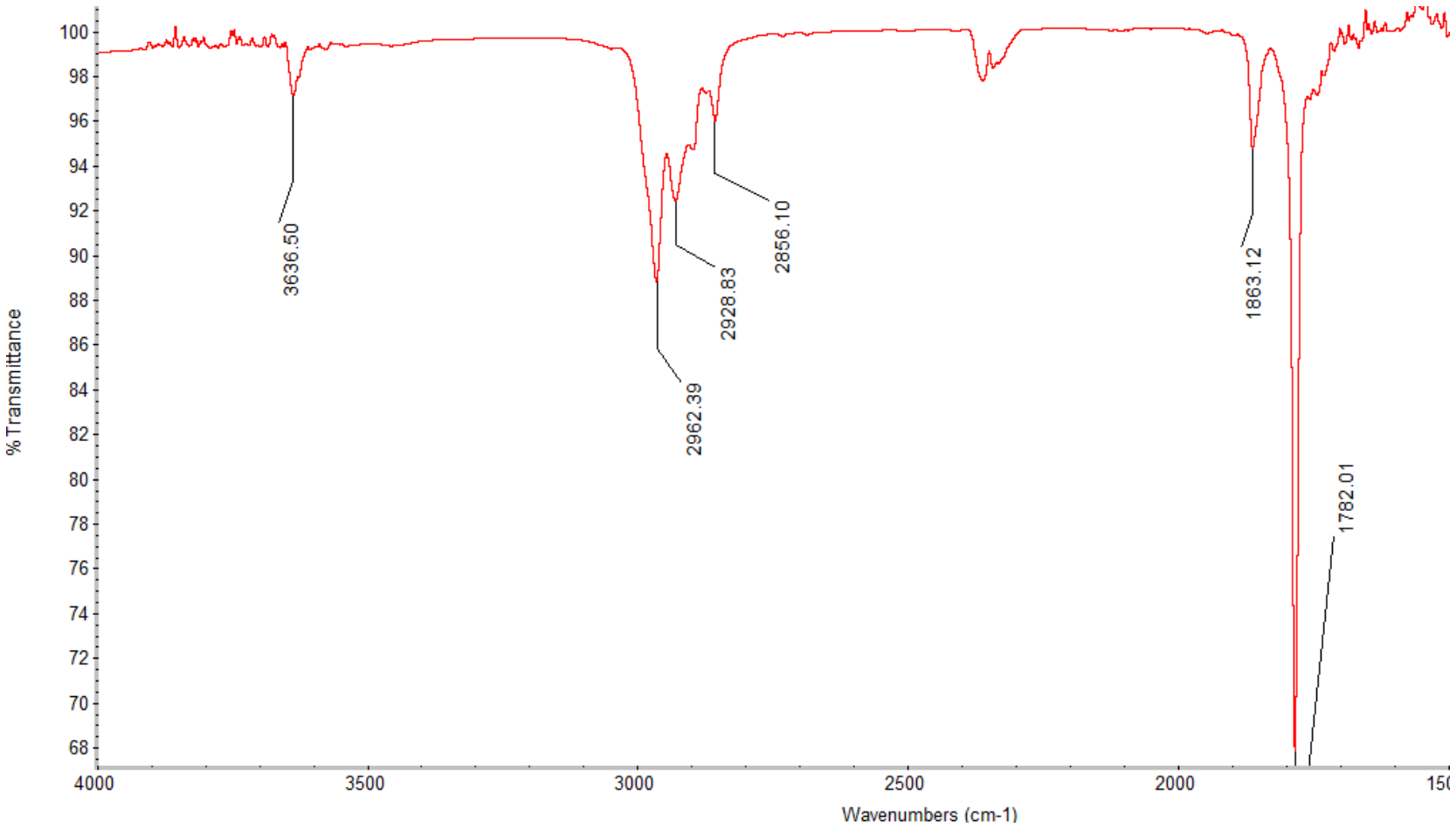
9

^{13}C spectrum of **9**

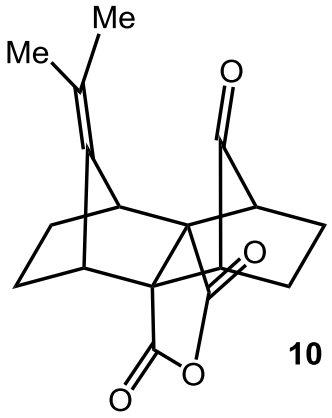


9

IR spectrum of **9** (CCl_4)

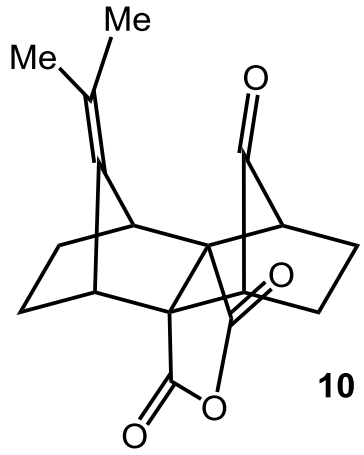


^{1}H spectrum of **10**



10

^{13}C spectrum of **10**

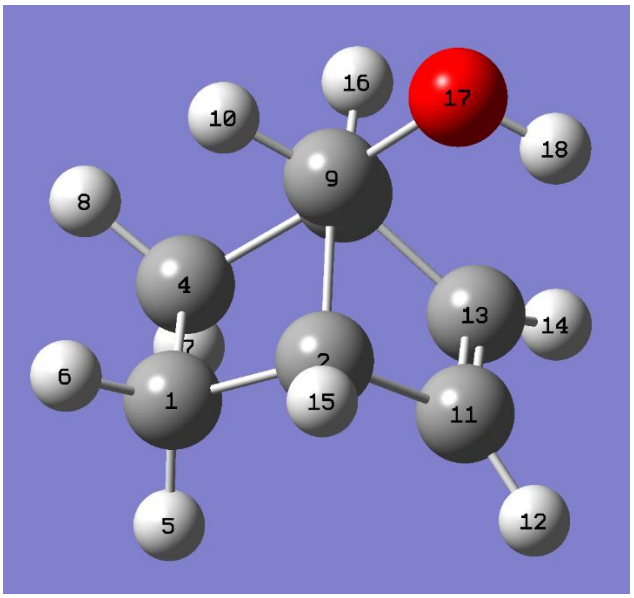


10

Molecular Modeling Calculations:

Standard orientation coordinates are included for each calculation. Atoms in molecules (AIM) calculations were performed using the coordinates of the structures optimized to ωB97XD/cc-pVTZ.

Equilibrium geometry at ωB97XD/cc-pVTZ for *syn*-7-norbornenol



opt freq rwb97xd/cc-pvtz maxdisk=12GB geom=connectivity

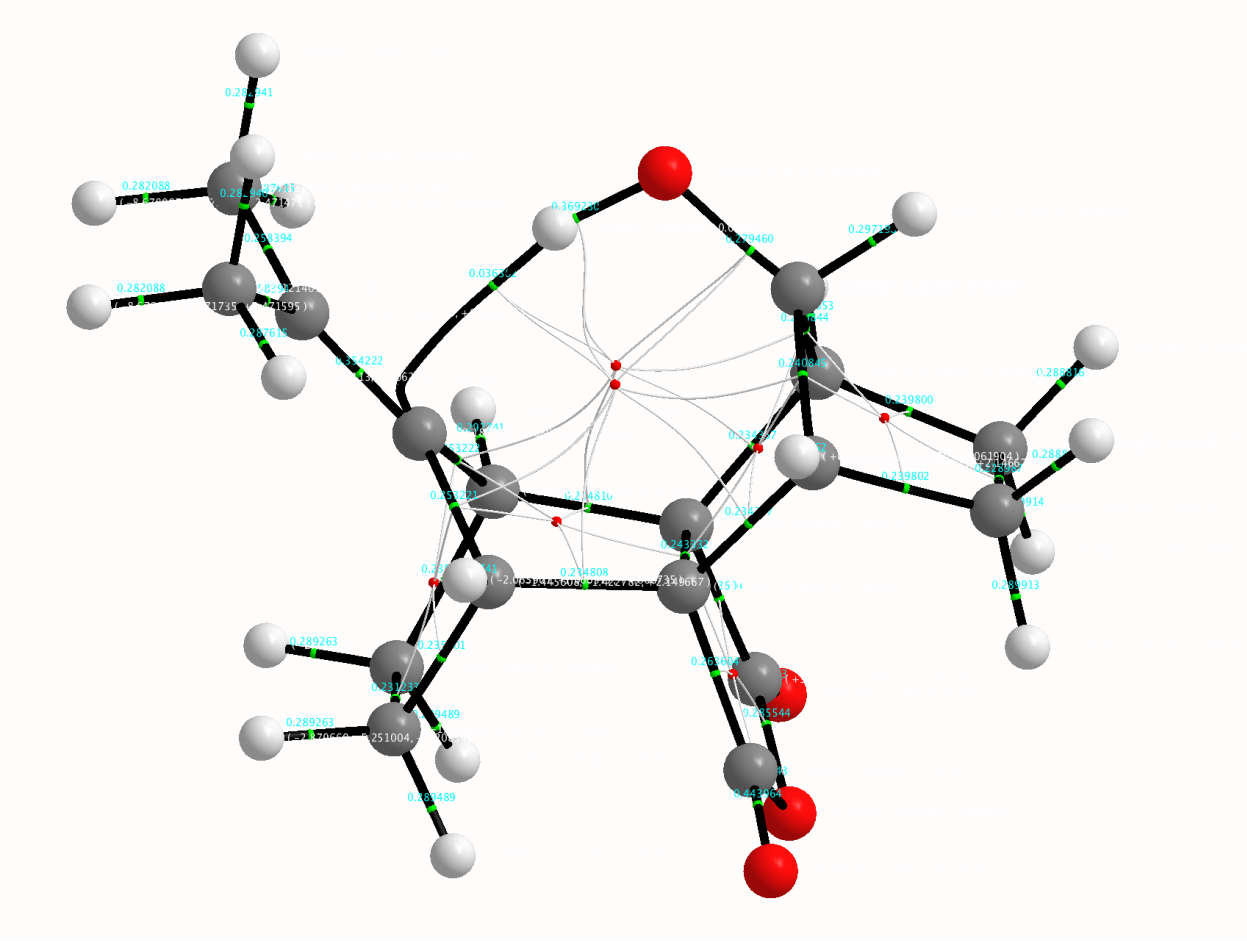
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.493714	-0.473030	-0.777181
2	6	0	-0.039566	-0.057201	-1.125235
3	6	0	-0.039700	-0.057987	1.125266
4	6	0	-1.493808	-0.473318	0.776801
5	1	0	-2.222990	0.216653	-1.196648
6	1	0	-1.707528	-1.465687	-1.172872
7	1	0	-2.222813	0.216762	1.196146
8	1	0	-1.708518	-1.465886	1.172197
9	6	0	0.723434	-0.790343	-0.000195
10	1	0	0.525385	-1.862566	-0.000598
11	6	0	0.116224	1.376269	-0.665812
12	1	0	0.116195	2.239260	-1.315448
13	6	0	0.116162	1.375817	0.666572
14	1	0	0.116076	2.238227	1.317001
15	1	0	0.270220	-0.278714	-2.142407
16	1	0	0.270158	-0.280032	2.142290

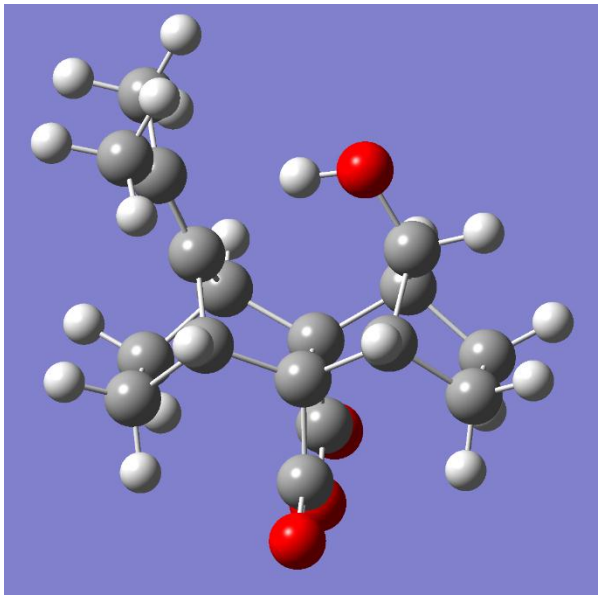
17	8	0	2.114735	-0.655522	0.000101
18	1	0	2.311744	0.284912	-0.001761

Frequencies --	3210.6740			3235.8255			3845.7400		
Red. masses --	1.0867			1.1066			1.0646		
Frc consts --	6.5999			6.8269			9.2768		
IR Inten --	6.6357			12.7201			22.6238		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
17 8	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.00
18 1	0.00	0.00	0.00	0.00	0.00	0.00	-0.23	-0.97	0.00

AIM calculated structure for 1



Equilibrium geometry at ωB97XD/cc-pVTZ for 1



freq wb97xd/cc-pvtz maxdisk=29GB geom=connectivity

Standard orientation:

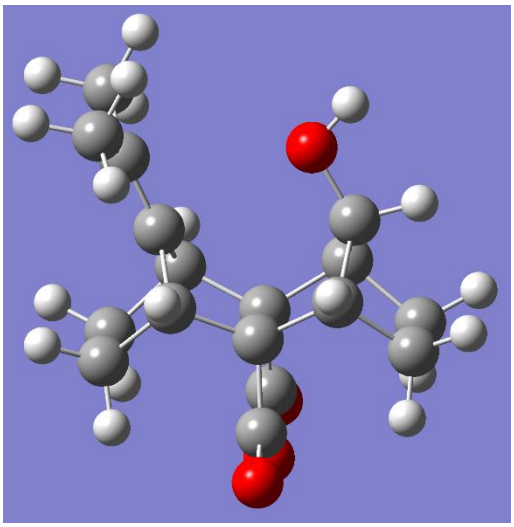
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.782725	1.450756	-1.136176
2	6	0	2.237296	1.826412	0.782249
3	6	0	0.567329	-0.043614	0.772817
4	6	0	0.782568	1.450963	1.135969
5	6	0	0.567354	-0.043746	-0.772798
6	6	0	2.237420	1.826207	-0.782312
7	1	0	2.977977	1.149643	1.201313
8	1	0	2.463005	2.815569	-1.174991
9	1	0	0.485856	1.705342	-2.149761
10	1	0	2.462767	2.815887	1.174710
11	1	0	0.485544	1.705713	2.149467
12	1	0	2.978135	1.149293	-1.201085
13	6	0	0.091847	2.250262	-0.000223
14	1	0	0.504664	3.259295	-0.000281
15	6	0	-0.764983	-0.752904	1.137555
16	1	0	-1.093228	-0.561445	2.153082
17	6	0	-0.764994	-0.752993	-1.137486
18	1	0	-1.093231	-0.561590	-2.153026
19	6	0	1.762338	-0.892379	-1.145571
20	8	0	2.168304	-1.190580	-2.220278
21	6	0	1.762414	-0.892026	1.145772
22	8	0	2.168050	-1.190465	2.220537

23	8	0	2.395187	-1.337011	0.000147
24	6	0	-0.651654	-2.257105	0.780369
25	1	0	-1.523855	-2.778712	1.168606
26	1	0	0.226331	-2.738384	1.206384
27	6	0	-0.651713	-2.257170	-0.780200
28	1	0	-1.523962	-2.778772	-1.168334
29	1	0	0.226224	-2.738513	-1.206238
30	6	0	-1.686619	-0.360025	0.000022
31	6	0	-2.980981	-0.051636	0.000009
32	6	0	-3.768483	0.148956	1.263211
33	1	0	-4.592258	-0.567138	1.307912
34	1	0	-3.168773	0.033214	2.161893
35	1	0	-4.214563	1.145697	1.278288
36	6	0	-3.768483	0.148822	-1.263213
37	1	0	-4.592246	-0.567290	-1.307846
38	1	0	-4.214578	1.145554	-1.278394
39	1	0	-3.168767	0.032999	-2.161880
40	8	0	-1.282029	2.459092	-0.000339
41	1	0	-1.741431	1.612665	-0.000319

Frequencies --	3174.7954	3176.5367	3736.0023
Red. masses --	1.0888	1.0904	1.0655
Frc consts --	6.4659	6.4823	8.7624
IR Inten --	36.6059	0.4024	468.9632

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
40	8	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.05	0.00
41	1	0.00	0.00	0.00	0.00	0.00	0.00	-0.50	-0.87	0.00

Energy Calculation at ωB97XD/cc-pVTZ for non-hydrogen bound 1

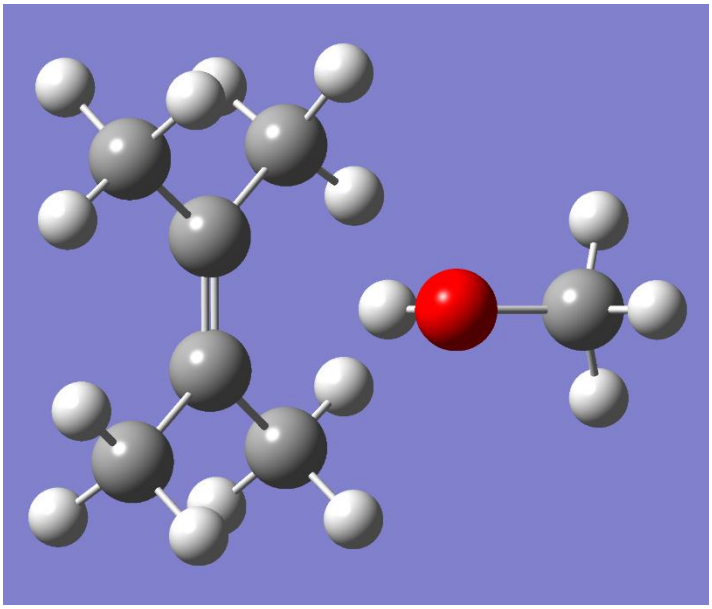


wb97xd/cc-pvtz maxdisk=12GB geom=connectivity

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.770143	1.445046	-1.136042
2	6	0	2.221875	1.831404	0.782408
3	6	0	0.565966	-0.051080	0.772808
4	6	0	0.770004	1.445032	1.136103
5	6	0	0.565979	-0.051063	-0.772807
6	6	0	2.221987	1.831351	-0.782153
7	1	0	2.967609	1.160163	1.201401
8	1	0	2.440150	2.822413	-1.174739
9	1	0	0.471367	1.697498	-2.149601
10	1	0	2.439929	2.822503	1.174962
11	1	0	0.471088	1.697452	2.149627
12	1	0	2.967750	1.160046	-1.200997
13	6	0	0.073304	2.239243	-0.000007
14	1	0	0.478549	3.251341	0.000029
15	6	0	-0.760992	-0.770368	1.137488
16	1	0	-1.090653	-0.581471	2.153036
17	6	0	-0.761021	-0.770237	-1.137553
18	1	0	-1.090691	-0.581201	-2.153072
19	6	0	1.767284	-0.890683	-1.145671
20	8	0	2.175464	-1.185731	-2.220410
21	6	0	1.767377	-0.890550	1.145672
22	8	0	2.175246	-1.186045	2.220405
23	8	0	2.403456	-1.330672	-0.000001
24	6	0	-0.636399	-2.273643	0.780156
25	1	0	-1.504664	-2.801807	1.168349
26	1	0	0.245171	-2.748371	1.206118
27	6	0	-0.636470	-2.273558	-0.780413
28	1	0	-1.504790	-2.801643	-1.168591
29	1	0	0.245045	-2.748269	-1.206504
30	6	0	-1.685555	-0.384295	0.000000
31	6	0	-2.982191	-0.085613	0.000026
32	6	0	-3.771163	0.108952	1.263254
33	1	0	-4.589550	-0.613298	1.307892
34	1	0	-3.170595	-0.002380	2.161920
35	1	0	-4.224699	1.102321	1.278430
36	6	0	-3.771183	0.109061	-1.263170
37	1	0	-4.589558	-0.613198	-1.307866
38	1	0	-4.224734	1.102424	-1.278252
39	1	0	-3.170624	-0.002179	-2.161853
40	8	0	-1.302098	2.437774	-0.000093
41	1	0	-1.496320	3.381048	-0.000095

Equilibrium geometry at ωB97XD/cc-pVTZ for 2



opt wb97xd/cc-pvtz maxdisk=21GB geom=connectivity

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.849131	0.697204	0.233716
2	6	0	0.953160	-0.637631	0.177646
3	8	0	-1.949905	0.013952	-1.143646
4	6	0	-2.831534	-0.151978	-0.059384
5	1	0	-3.845816	-0.105542	-0.453147
6	1	0	-2.702662	-1.119665	0.438123
7	1	0	-2.721690	0.637310	0.692620
8	1	0	-1.049673	-0.017812	-0.804544
9	6	0	1.395818	1.633941	-0.812301
10	1	0	1.916753	2.463847	-0.330166
11	1	0	2.087686	1.169797	-1.507896
12	1	0	0.575954	2.071083	-1.388676
13	6	0	1.616866	-1.387467	-0.947452
14	1	0	2.494656	-1.924058	-0.578533
15	1	0	0.930872	-2.141725	-1.340582
16	1	0	1.926725	-0.762180	-1.778258
17	6	0	0.412230	-1.576122	1.224145
18	1	0	-0.367678	-2.211133	0.794891
19	1	0	1.204287	-2.247604	1.563821
20	1	0	0.000559	-1.082606	2.098672
21	6	0	0.146406	1.447139	1.334769
22	1	0	-0.401295	0.815059	2.026710
23	1	0	0.862895	2.039136	1.909570

24	1	0	-0.564784	2.153960	0.899729

Frequencies --	3177.8961	3178.8871	3788.8611
Red. masses --	1.0930	1.0929	1.0668
Frc consts --	6.5034	6.5072	9.0233
IR Inten --	48.3966	3.9820	338.4017

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
3	8	0.00	0.00	0.00	0.00	0.00	0.00	-0.06	0.00	-0.02
8	1	0.00	0.00	0.00	0.00	0.00	0.00	0.94	-0.03	0.34

Equilibrium geometry at ωB97XD/cc-pVTZ for Methanol

opt freq b3lyp/cc-pvtz maxdisk=15GB geom=connectivity

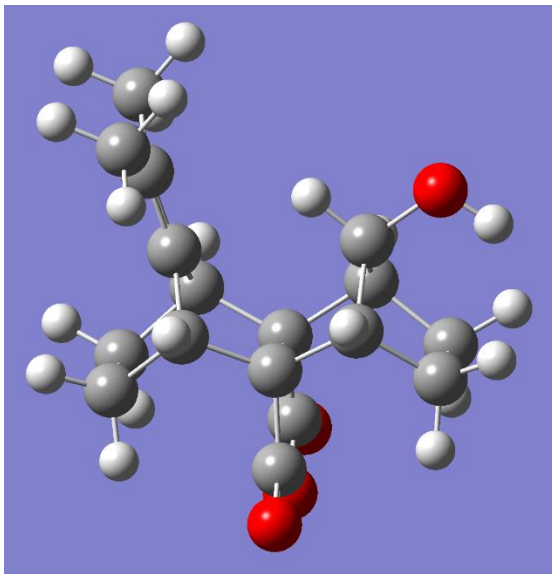
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.664866	-0.020024	0.000000
2	1	0	1.083605	0.985097	-0.000001
3	1	0	1.030345	-0.543067	-0.890184
4	1	0	1.030345	-0.543065	0.890185
5	8	0	-0.748847	0.121950	0.000000
6	1	0	-1.142722	-0.754419	0.000000

Frequencies --	3027.0903	3100.5450	3828.3237
Red. masses --	1.1051	1.0964	1.0665
Frc consts --	5.9662	6.2100	9.2093
IR Inten --	67.6305	30.1465	25.2290

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
5	8	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.06	0.00
6	1	0.00	0.00	0.00	0.00	-0.02	0.00	-0.42	-0.91	0.00

Equilibrium geometry at ωB97XD/cc-pVTZ for 9



opt freq wb97xd/cc-pvtz maxdisk=15GB geom=connectivity

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.664873	1.329876	1.135360
2	6	0	-2.099357	1.773411	-0.779643
3	6	0	-0.496934	-0.163722	-0.775123
4	6	0	-0.664963	1.329917	-1.135299
5	6	0	-0.496895	-0.163761	0.775118
6	6	0	-2.099291	1.773396	0.779835
7	1	0	-2.863724	1.124620	-1.201083
8	1	0	-2.295363	2.765520	1.185526
9	1	0	-0.356116	1.573925	2.148074
10	1	0	-2.295532	2.765531	-1.185307
11	1	0	-0.356265	1.574004	-2.148022
12	1	0	-2.863638	1.124616	1.201326
13	6	0	0.123563	2.022866	0.000014
14	6	0	0.840711	-0.863790	-1.135546
15	1	0	1.164066	-0.669409	-2.152516
16	6	0	0.840725	-0.863887	1.135451
17	1	0	1.164099	-0.669569	2.152421
18	6	0	0.738230	-2.365718	-0.779454
19	1	0	1.613004	-2.882552	-1.168203
20	1	0	-0.137931	-2.851781	-1.205274
21	6	0	0.738210	-2.365788	0.779248
22	1	0	1.612960	-2.882674	1.167977
23	1	0	-0.137976	-2.851865	1.205000

24	6	0	1.747626	-0.430216	-0.000041
25	6	0	-1.702260	-0.993691	1.147013
26	8	0	-2.120400	-1.277160	2.221060
27	6	0	-1.702278	-0.993689	-1.147006
28	8	0	-2.120476	-1.277084	-2.221053
29	8	0	-2.335718	-1.435050	0.000002
30	6	0	2.992081	0.025620	-0.000002
31	1	0	1.174432	1.772997	-0.000037
32	8	0	0.093449	3.425832	0.000041
33	1	0	-0.811048	3.738816	-0.000286
34	6	0	3.745194	0.334738	1.261911
35	1	0	4.698165	-0.198768	1.279587
36	1	0	3.981146	1.401268	1.309177
37	1	0	3.194212	0.072420	2.161504
38	6	0	3.745096	0.335122	-1.261869
39	1	0	3.981450	1.401603	-1.308493
40	1	0	4.697863	-0.198722	-1.280030
41	1	0	3.193846	0.073616	-2.161540

Frequencies --	3169.2825	3215.3461	3902.6614
Red. masses --	1.0898	1.0870	1.0654
Frc consts --	6.4495	6.6211	9.5602
IR Inten --	1.6843	5.6146	18.9064

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
32	8	0.00	0.00	0.00	0.00	0.00	0.00	-0.06	0.02	0.00
33	1	0.00	0.00	0.00	-0.02	0.00	0.00	0.94	-0.34	0.00