Supplementary Information file for paper

Toluene and benzyl decomposition mechanisms: elementary reactions and kinetic simulations

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This file contains

Thermochemical data of key species used in the kinetic simulations. Quantitative analysis of the relevance of different reaction channels to the production of atomic H. Chebyshev fits of the C_7H_7 and C_7H_5 decomposition kinetic constants. Branching ratios for the decomposition of C_7H_5. Details about hindered rotors calculations. Structures, vibrational frequencies and inertia moments for the wells and saddle points of the C_7H_7 and C_7H_5 potential energy surface located at the B3LYP/6-31+G(d,p) level and used in the RRKM/ME calculations.

TABLE S1. Thermochemical data used for the kinetic simulations.

species	$\Delta H_f^0{}_{298K}$ [kcal/mol]	S_{298K} [cal/(mol K)]
$C_6H_5CH_3$	11.95[a]	76.52[a]
$C_6H_5CH_2$	49.00[b,c]	76.04[d]
C_7H_6	78.90	75.70
C_7H_5	108.1	77.00

[a]Thermodynamic data used for toluene and for all the other species not listed into the table are from the database of Burcat and Ruscic: Burcat A.; Ruscic B., Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with updates from Active Thermochemical Tables, ANL-05/20 and TAE 960 Technion–IIT, Aerospace Engineering, and Argonne National Laboratory, Chemistry Division, September 2005; ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics;
[b]Sivaramakrishnan, R.; Tranter, R.S.; Brezinsky, K. J. Phys. Chem.A 2006, 110, 9388-9399;
[c]Braun-Unkhoff, M.; Frank, P.; Just, T. H. Ber. Bunsen-Ges. Phys.Chem. 1990, 94, 1417-1425;
[d]Ruscic, B.; Boggs, J.E.; Burcat, A.; Csaszar, A.G.; Demaison, J.; Janoschek, R.; Martin, J.M.L.; Morton, M.; Rossi, M.J.; Stanton, J.F.; Szalay, P.G.; Westmoreland, P.R.; Zabel, F.; Berces, T. J. Phys. Chem. Ref. Data 2005, 34, 573-656.

Table S2. Decomposition pathways for selected species at 1573 K and 0.67 bar calculated for the simulations of the experimental data of Figure 7.

Species	Reactions	Contribution[a,b] (%)
$C_6H_5CH_2$	$C_6H_5CH_2 \leftrightarrow C_7H_6 + H$	50.8
	$C_6H_5CH_2 \leftrightarrow o\text{-}C_6H_4 + CH_3$	48.5
C_7H_6	$C_7H_6 \leftrightarrow C_7H_5 + H$	53.6
	$C_7H_6 \leftrightarrow C_5H_4 + C_2H_2$	40.1
C_7H_5	$C_7H_5 \leftrightarrow C_4H_2 + C_3H_3$	81.3
	$C_7H_5 \leftrightarrow C_5H_3 + C_2H_2$	16.2
$o\text{-}C_6H_4$	$o\text{-}C_6H_4 \leftrightarrow C_4H_2 + C_2H_2$	71.0

[a]Percentage contribution of the reaction to the species production/consumption rate.
[b]Only reactions with contribution higher than 10% are reported.

Table S3. Production pathway for H atoms at 1573 K and 0.67 bar calculated for the simulations of the experimental data of Figure 7.

Species	Reactions	Contribution[a] (%)
H	$C_6H_5CH_2 \leftrightarrow C_7H_6 + H$	65.1
	$C_7H_6 \leftrightarrow C_7H_5 + H$	34.9

[a]Percentage contribution of the reaction to the species production rate.

Table S4. Decomposition pathways for selected species at 1602 K and 1.6 bar calculated for the simulations of the experimental data of Figure 9b.

Species	Reactions	Contribution[a,b] (%)
$C_6H_5CH_3$	$C_6H_5CH_3 \leftrightarrow C_6H_5CH_2 + H$	83.2
	$C_6H_5CH_3 \leftrightarrow C_6H_5 + CH_3$	11.4
$C_6H_5CH_2$	$C_6H_5CH_2 \leftrightarrow C_7H_6 + H$	55.3
	$C_6H_5CH_2 \leftrightarrow o\text{-}C_6H_4 + CH_3$	44.7
C_7H_6	$C_7H_6 \leftrightarrow C_7H_5 + H$	54.1
	$C_7H_6 \leftrightarrow C_5H_4 + C_2H_2$	31.6
C_7H_5	$C_7H_5 \leftrightarrow C_4H_2 + C_3H_3$	78.9
	$C_7H_5 \leftrightarrow C_5H_3 + C_2H_2$	15.8
C_6H_5	$C_6H_5 \leftrightarrow o\text{-}C_6H_4 + H$	49.8
	$C_6H_5 + H \leftrightarrow C_6H_6$	40.2
$o\text{-}C_6H_4$	$o\text{-}C_6H_4 \leftrightarrow C_4H_2 + C_2H_2$	83.9
C_5H_5	$C_5H_5 \leftrightarrow C_3H_3 + C_2H_2$	98.3

[a]Percentage contribution of the reaction to the species production/consumption rate.
[b]Only reactions with contributions higher than 10% are reported.

Table S5. Production pathways for H atoms at 1602 K and 1.6 bar calculated for the simulations of the experimental data of Figure 9b.

Species	Reactions	Contribution[a] (%)
H	$C_6H_5CH_3 \leftrightarrow C_6H_5CH_2 + H$	51.1
	$C_6H_5CH_2 \leftrightarrow C_7H_6 + H$	29.2
	$C_7H_6 \leftrightarrow C_7H_5 + H$	15.8
	$C_6H_5 \leftrightarrow o\text{-}C_6H_4 + H$	3.9

[a]Percentage contribution of the reaction to the species production rate.

Chebyshev interpolation of pressure dependent kinetic constants

The Chebyshev expansion methodology proposed by Venkatesh et al.[a] for approximating the pressure and temperature dependence of multiple-well reactions was used to fit the kinetic constants of C_7H_7 and C_7H_5 decomposition reactions. The Chebyshev expansions approximate the logarithm of the rate coefficient directly as a truncated bivariate Chebyshev series in the reverse temperature and logarithm of the pressure. Each reaction was fitted using 6 temperatures functions along the temperature axis and 4 pressure functions along the pressure axis, thus leading to 6x4 Chebyshev coefficients. The fitted kinetic constants are reported below in the Chemkin format[b].

REACTION A b E

2. $C_6H_5CH_2(+M) \leftrightarrow C_7H_6 + H(+M)$ 1.00E+00 0.0 0.0
Chebychev temperature limits, tmin= 0.150E+04, tmax= 0.200E+04
Chebychev pressure limits, pmin= 0.130E-01, pmax= 0.100E+02
CHEB/ 6 4 4.0937 0.4746 -0.0794 0.0103/
CHEB/ -5.2742 -0.7359 0.0923 0.0084 1.1220/
CHEB/ 0.2821 -0.0027 -0.0155 0.0686 -0.0072/
CHEB/ -0.0104 -0.0064 -0.0010 -0.0050 -0.0043/
CHEB/ -0.0017 -0.0027 -0.0003 0.0036 0.0028/

3. $C_6H_5CH_2(+M) \leftrightarrow o\text{-}C_6H_4 + CH_3(+M)$ 1.00E+00 0.0 0.0
Chebychev temperature limits, tmin= 0.150E+04, tmax= 0.200E+04
Chebychev pressure limits, pmin= 0.130E-01, pmax= 0.100E+02
CHEB/ 6 4 4.0750 0.5224 -0.0818 0.0093/
CHEB/ -5.2765 -0.7755 0.1089 0.0126 1.1450/
CHEB/ 0.2773 -0.0227 -0.0187 0.0653 -0.0203/
CHEB/ -0.0100 -0.0039 -0.0023 -0.0038 -0.0085/
CHEB/ -0.0072 -0.0019 0.0079 -0.0005 -0.0024/

9. $C_7H_5(+M) \leftrightarrow C_5H_3 + C_2H_2(+M)$ 1.00E+00 0.0 0.0
Chebychev temperature limits, tmin= 0.150E+04, tmax= 0.200E+04
Chebychev pressure limits, pmin= 0.130E-01, pmax= 0.100E+02
CHEB/ 6 4 3.3519 1.1919 -0.1456 -0.1783/
CHEB/ -4.3307 -1.5506 0.1348 0.2422 0.9339/
CHEB/ 0.3711 0.0192 -0.0667 0.0431 -0.0156/
CHEB/ -0.0159 -0.0001 -0.0050 -0.0109 0.0038/
CHEB/ 0.0027 0.0016 0.0079 0.0030 -0.0005/

10. $C_7H_5(+M) \leftrightarrow C_4H_2 + C_3H_3(+M)$ 1.00E+00 0.0 0.0
Chebychev temperature limits, tmin= 0.150E+04, tmax= 0.200E+04
Chebychev pressure limits, pmin= 0.130E-01, pmax= 0.100E+02
CHEB/ 6 4 4.3433 1.0193 -0.1408 -0.1454/
CHEB/ -5.2954 -1.3423 0.1355 0.2028 0.9059/
CHEB/ 0.3378 0.0124 -0.0608 0.0508 -0.0081/
CHEB/ -0.0071 0.0025 -0.0012 -0.0031 -0.0006/
CHEB/ 0.0007 -0.0008 -0.0001 0.0004 -0.0003/

[a]Venkatesh, P. K.; Chang, A.Y.; Dean, A.M.; Cohen, M. H.; Carr, R.W. AIChE J. 1997, 43, 1331-1340

[b]It was verified that the Chebyshev approximation can lead to inaccurate predictions of the kinetic constants for reactions (2) and (3) in the 0.1-1 bar pressure range at low temperatures.

Branching Ratios for the decomposition of C_7H_5

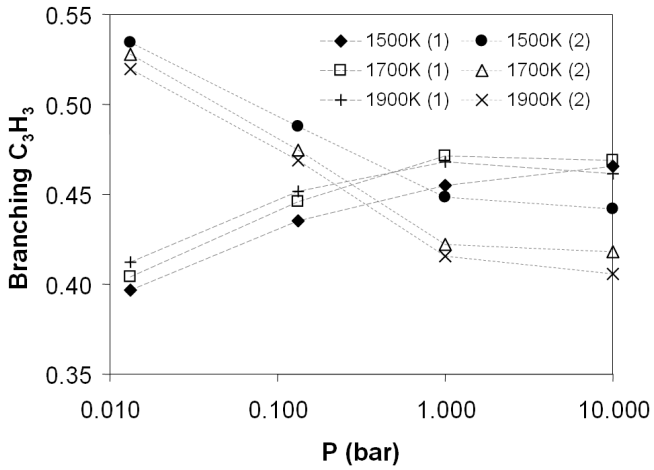


Figure S1. Branching ratio for the production of C_3H_3 + C_4H_2 given separately as a function of pressure and temperature for channel (1), which involves intermediates **4** and **5,** and channel (2), which involves intermediates **6** and **7.**

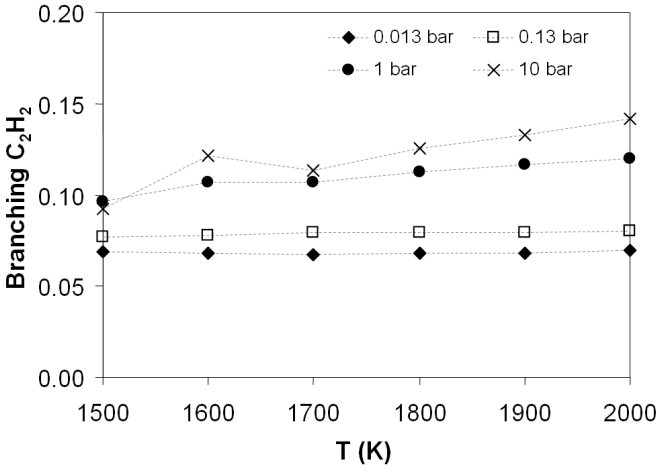


Figure S2. Branching ratio for the production of C_2H_2 + C_5H_3 as a function of pressure and temperature.

Hindered Rotors PES and inertia moments

The analysis of the low vibrational frequencies of all the wells and transition states considered in the calculations revealed that six vibrational motions should be treated as hindered rotors. These are the torsional vibrations of **W3** (64.7 cm^{-1}), **W5** (70.6 cm^{-1}), **W7** (41.7 cm^{-1}), **TS3** (29.1 cm^{-1}), **TS6** (16.0 cm^{-1}), and **TS9** (17.7 cm^{-1}). These internal motions correspond in all cases to rotations around the breaking bond.

The moments of inertia for the torsional rotations were calculated with respect to the rotating bond axis and reduced to account for the conjunct rotation of the two moieties as $I=I_1I_2/(I_1+I_2)$. The values so determined, reported in amuÅ^2, are 13.3 for **W3**, 20.0 for **TS3**, 60.9 for **W5**, 77.3 for **TS6**, 71.7 for **W7**, and 79.8 for **TS9**.

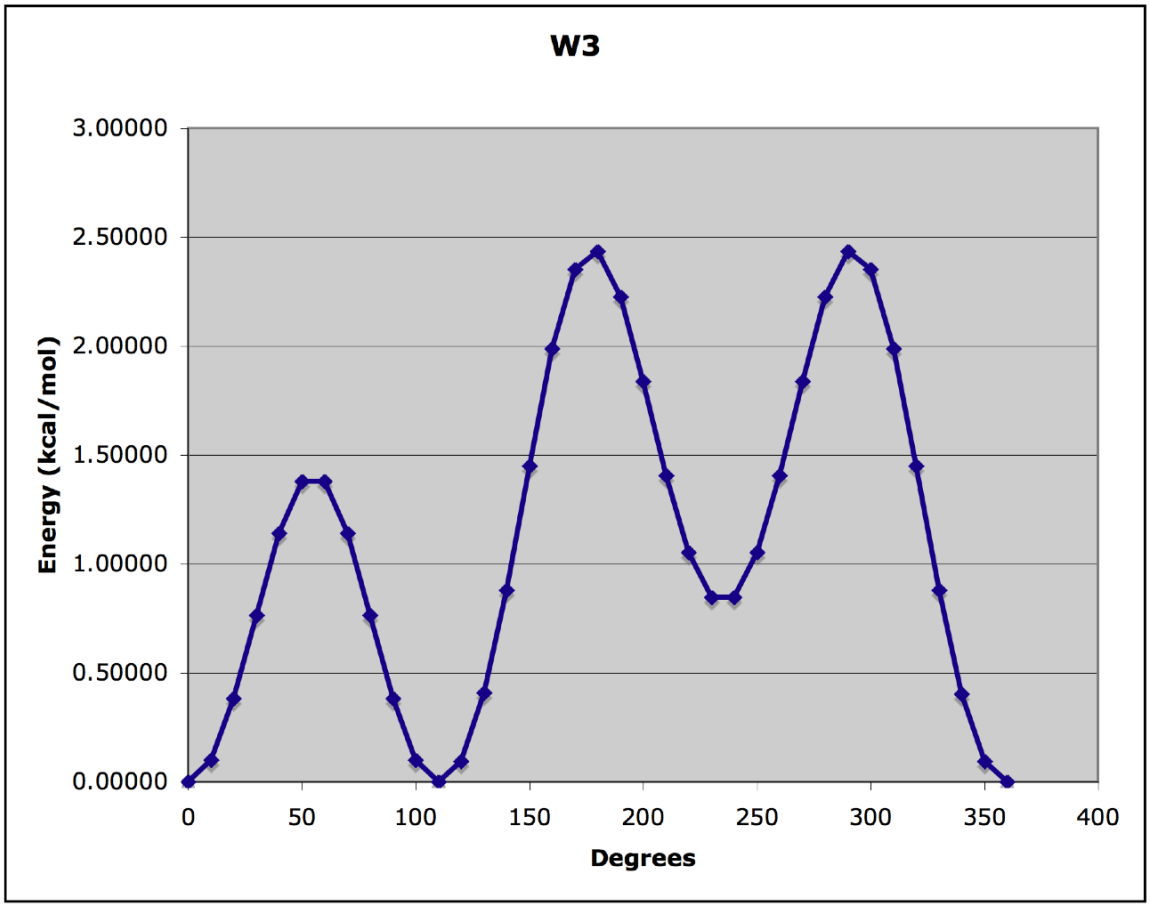


Figure S3. Torsional PES for **W3** calculated through a 36 step rotational scan at the B3LYP/6-31+G(d,p) level.

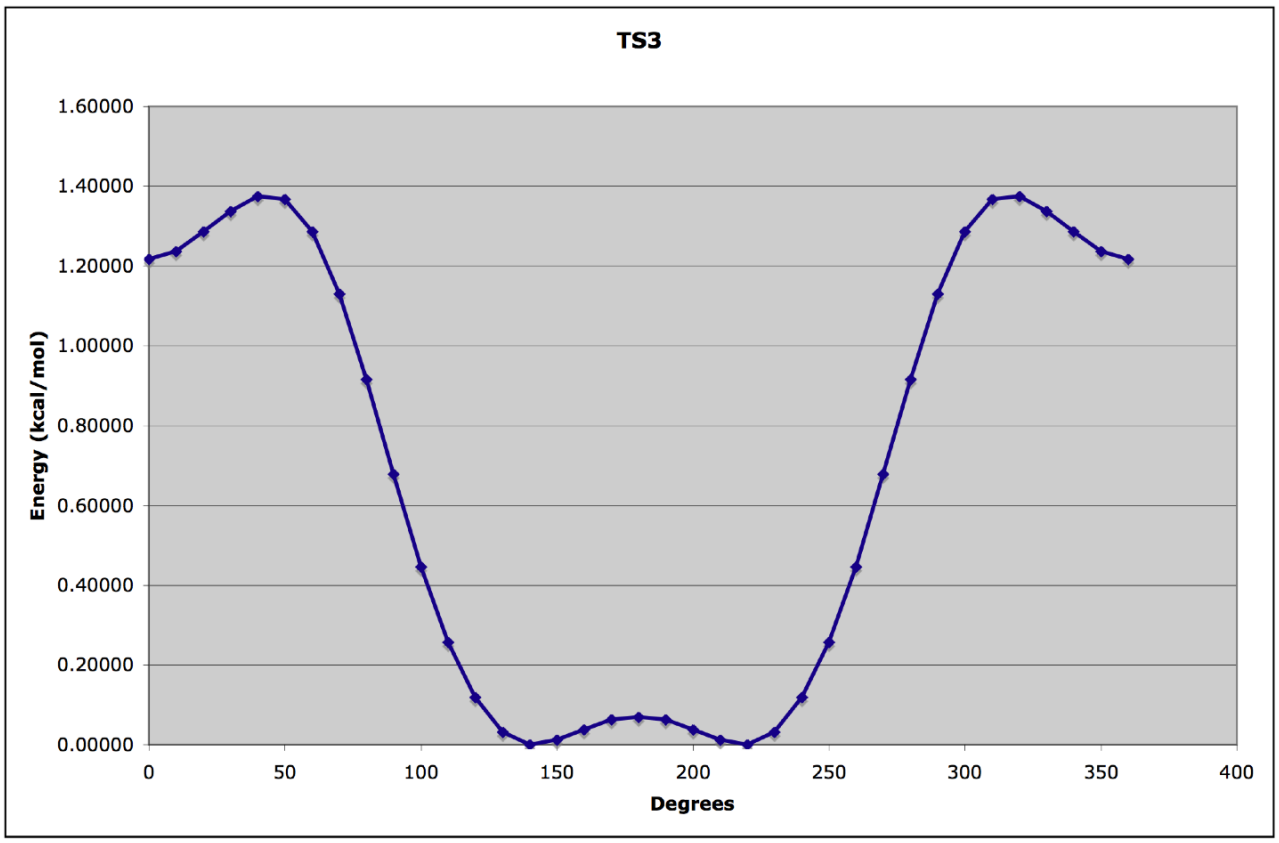


Figure S4. Torsional PES for **TS3** calculated through a 36 step rotational scan at the B3LYP/6-31+G(d,p) level.

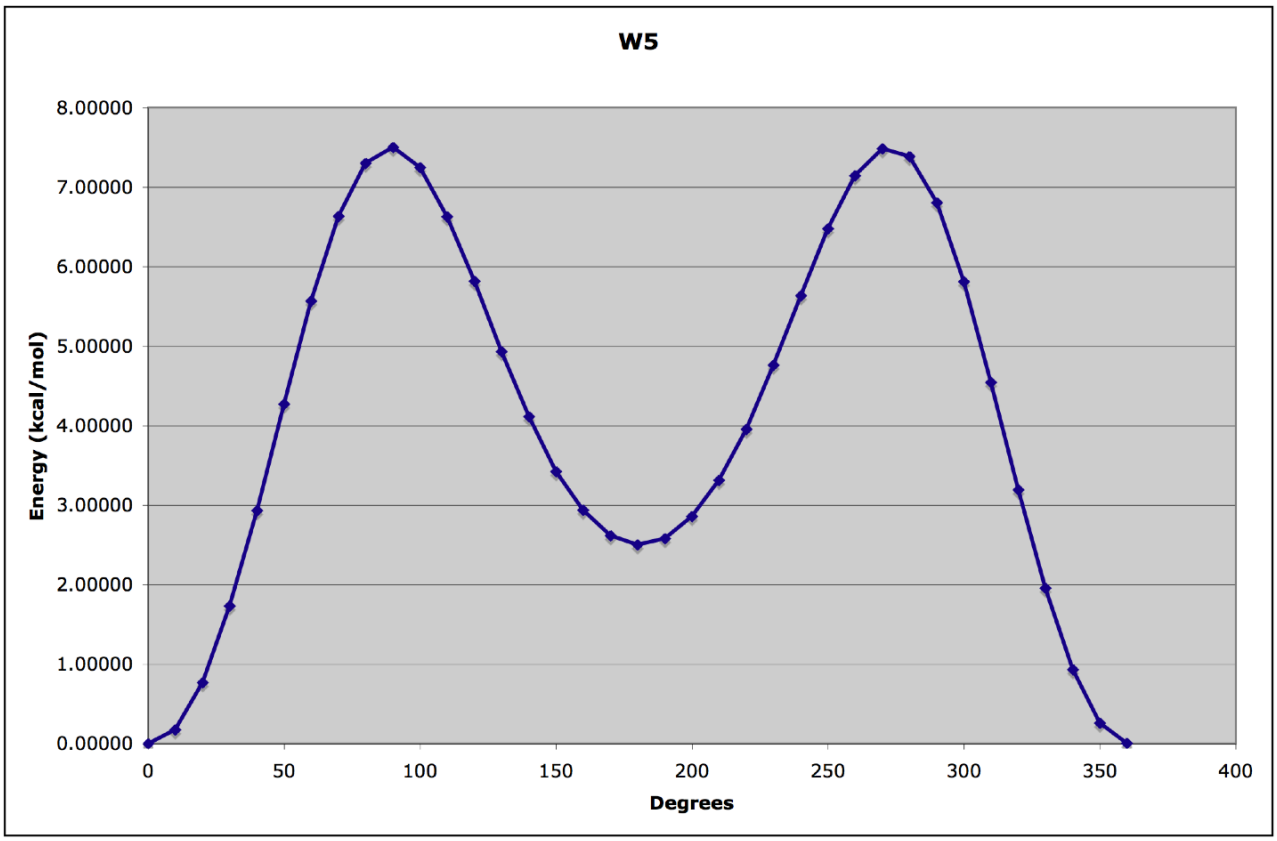


Figure S5. Torsional PES for **W3** calculated through a 36 step rotational scan at the B3LYP/6-31+G(d,p) level.

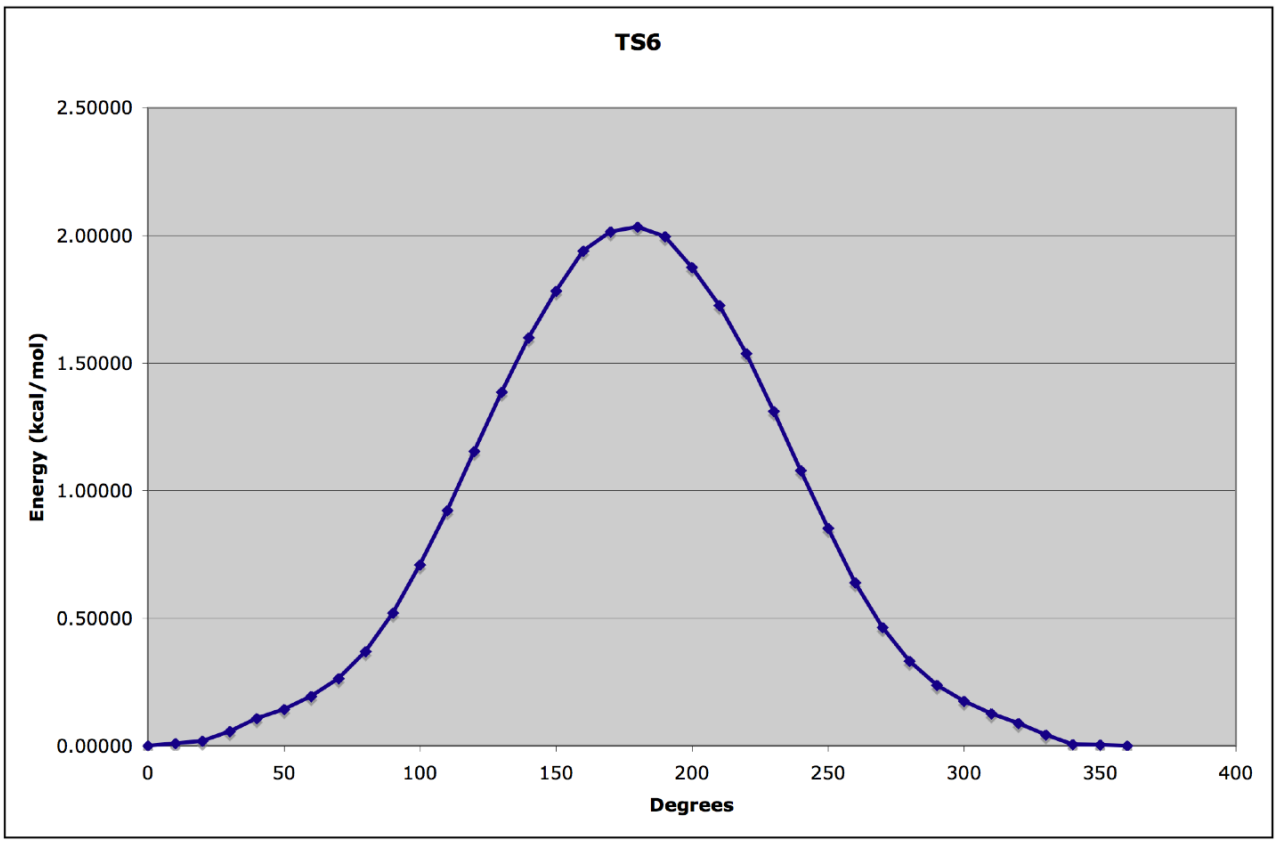


Figure S6. Torsional PES for **TS6** calculated through a 36 step rotational scan at the B3LYP/6-31+G(d,p) level.

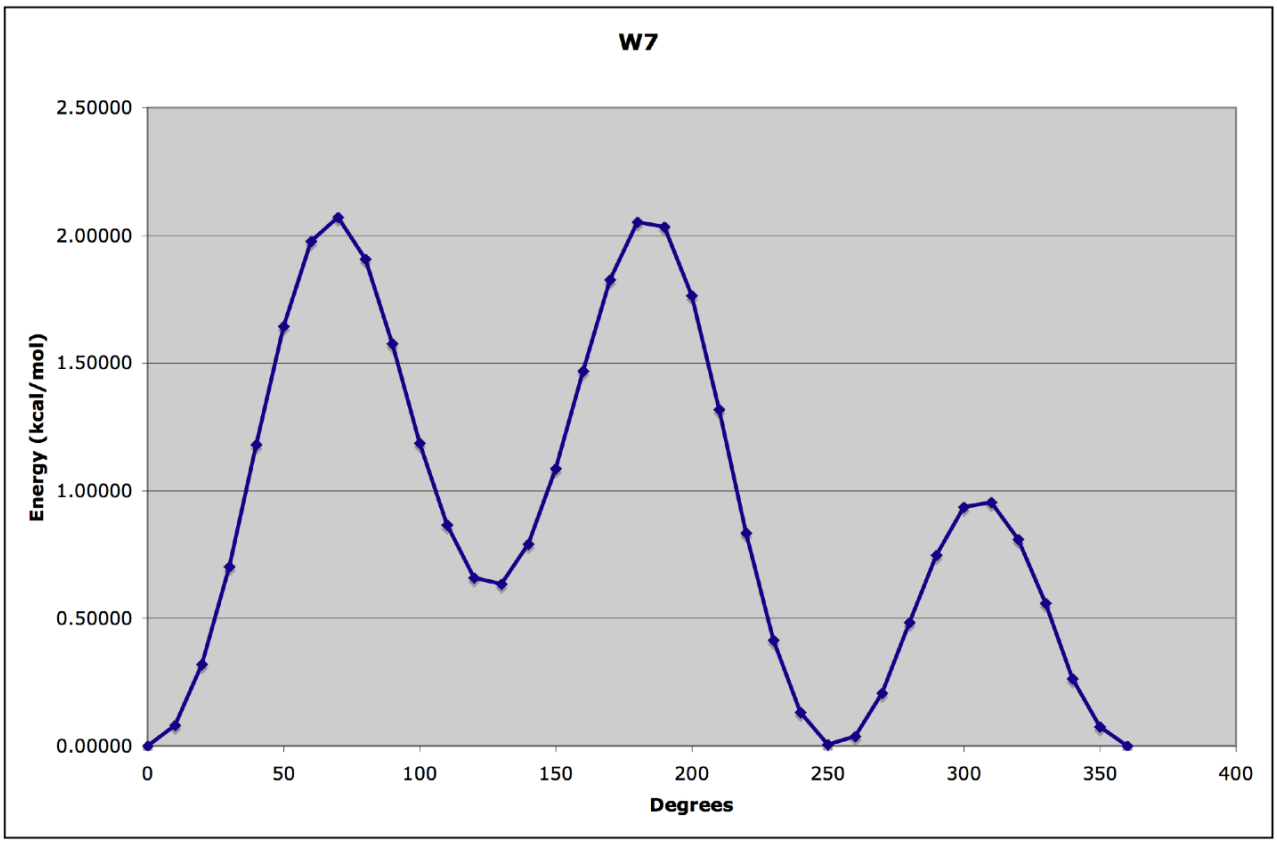


Figure S7. Torsional PES for **W7** calculated through a 36 step rotational scan at the B3LYP/6-31+G(d,p) level.

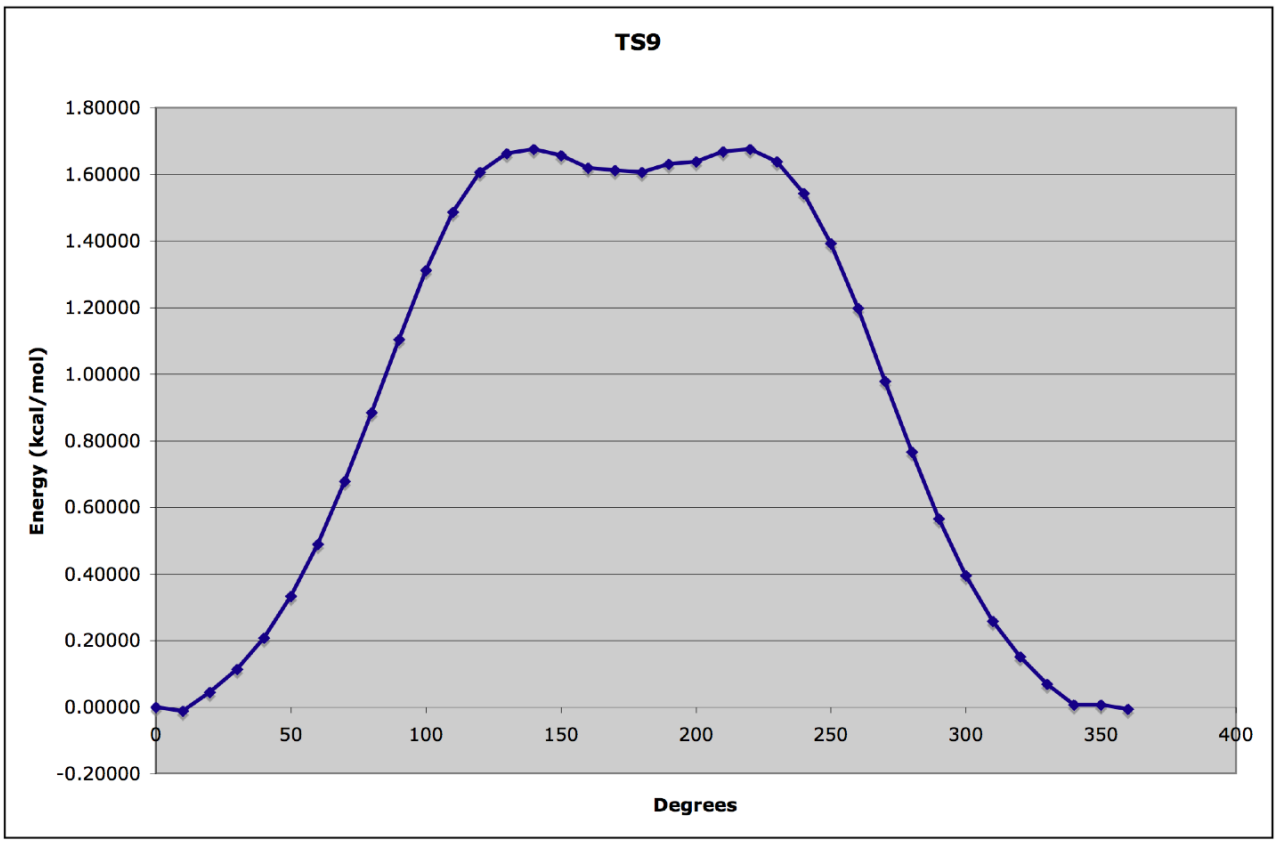
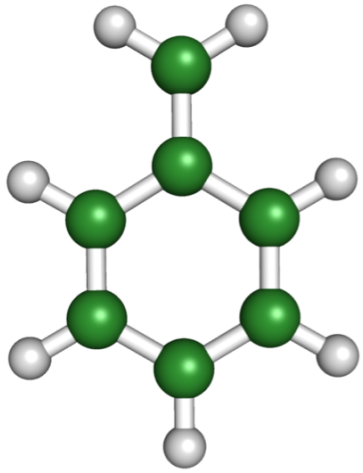


Figure S8. Torsional PES for **TS9** calculated through a 36 step rotational scan at the B3LYP/6-31+G(d,p) level.

C_7H_7 Potential Energy Surface

****
Wells
****

Well 1 Benzyl (C_7H_7)



C,0.8430004001,-0.271130289,-0.2295134511
C,-0.2785704228,-0.5479645311,-1.0695886473
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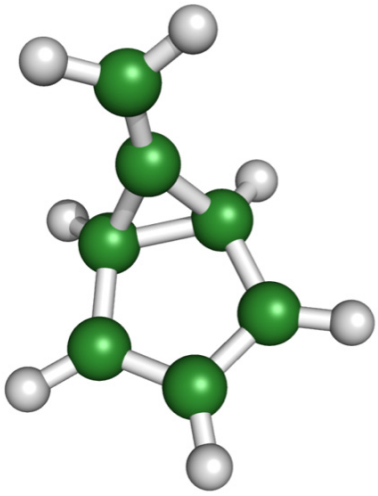
C,-1.7379676768,0.0229312868,0.8169376359
C,-0.6180824173,0.2882419238,1.6213494904
C,0.6709223288,0.1373199964,1.0853553677
C,-0.1100830738,-0.9635327162,-2.4046202822
H,-2.7373612749,0.1385843288,1.2272150751
H,-0.7479358229,0.6082764187,2.6507023191
H,1.5404975061,0.3415699554,1.7039144421
H,-2.4493336882,-0.5901413867,-1.1162318958
H,1.843611487,-0.3863903011,-0.6378285372
H,0.8789246653,-1.0857860647,-2.8332793109
H,-0.9649098974,-1.1723485603,-3.0390652119

Frequencies

199.9936	358.1659	392.5496
478.1927	501.3984	531.9975
625.7532	680.1926	711.3032
771.6701	829.9658	833.2717
900.6002	974.4286	975.0153
989.2378	992.6879	1037.5987
1118.4683	1176.9828	1188.5548
1290.8454	1340.1256	1357.1166
1476.9774	1498.0345	1509.5415
1582.8560	1604.1751	3162.9425
3175.4470	3177.7490	3189.8517
3194.6597	3207.6646	3261.0935

Rotational constants (GHZ): 5.52129 2.69173 1.80955

Well 2



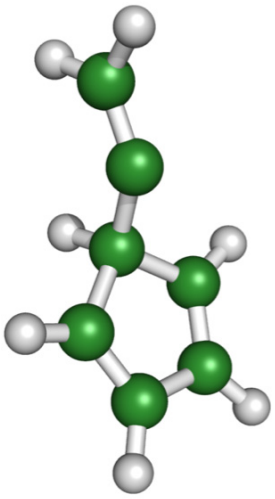
C,0.1957282965,-0.4202951213,0.9558269266
C,-0.1548749887,0.9846430031,0.3660828262
C,-1.2938470407,0.7227110774,-0.5597648485
C,-1.6036851533,-0.6377096752,-0.5651596399
C,-0.7773774442,-1.3456867553,0.3082678513
C,1.1300234809,0.3078285893,0.0625086
C,2.3243322304,0.3705802991,-0.5022933021
H,-1.7735368165,1.4898304346,-1.1561687247
H,2.6233804879,1.2308734658,-1.0968664826
H,-2.3636302581,-1.0911016643,-1.1929819385
H,-0.798844641,-2.4150723548,0.4823134742
H,-0.1318549969,1.8904775013,0.9702338451
H,3.0430112648,-0.4390172197,-0.3974037403
H,0.4796786739,-0.5584186655,1.9980630857

Frequencies

152.2598	237.6238	385.8456
441.0021	550.1502	619.5736
638.6509	683.5559	732.0473
747.7020	799.6725	874.9278
909.2691	916.2252	923.9392
973.5186	998.4022	1033.2350
1067.8858	1074.6488	1110.3587
1111.6154	1262.8978	1273.4008
1319.4955	1400.4694	1454.7831
1468.2623	1801.7475	3132.9776
3141.3757	3147.3969	3207.2478
3214.9190	3226.6602	3236.6488

Rotational constants (GHZ): 5.58578 2.50557 2.15845

Well 3



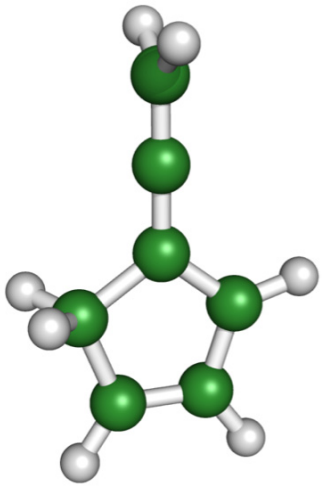
C,0.2947072359,-0.0737212792,0.4021301621
C,-0.6179327787,1.138806403,0.3576508718
C,-1.8495403786,0.7535371254,-0.0366750318
C,-1.8490733883,-0.6924901189,-0.3022520935
C,-0.6171568819,-1.1919265329,-0.0703638575
C,1.55320787,0.0670548617,-0.3618654204
C,2.8525246553,0.0296030919,-0.156489209
H,-2.7160609224,1.3970013273,-0.1432426291
H,3.5723656905,0.1773919033,-0.9588488846
H,-2.7151929524,-1.2566833427,-0.6305405173
H,-0.2870875752,-2.2172727546,-0.1813395776
H,-0.2883955693,2.1368851503,0.6180955346
H,3.2692931337,-0.1541204179,0.8408403561
H,0.5646601936,-0.2683831717,1.462223187

Frequencies

97.0886	124.9338	277.3584
313.5755	498.9011	511.2895
604.0503	699.0324	727.2156
808.3261	818.5097	870.5480
883.0708	954.8216	956.6023
962.9591	1008.8323	1012.1359
1073.5303	1109.8875	1137.8410
1196.7902	1213.0943	1309.8741
1401.4819	1420.3912	1561.2337
1645.7169	1732.8366	2903.0320
3052.6794	3178.4653	3210.3868
3221.5726	3244.6423	3248.8436

Rotational constants (GHZ): 7.25649 1.89060 1.58885

Well 4



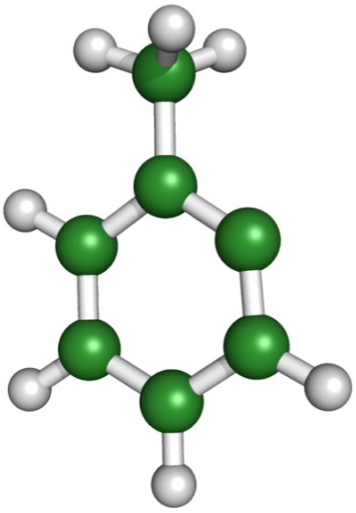
C,-0.1835398083,0.0383454857,-0.2592608049
C,-0.4048349344,-0.637148097,1.1023199979
C,0.9088943445,-0.4158009332,1.8078227498
C,1.7671606348,0.2808913742,0.9877228052
C,1.1510806168,0.5701953681,-0.255168301
C,-1.0830965715,0.1022360687,-1.2419033569
C,-1.9702253171,0.1609163575,-2.2006442283
H,1.1204834305,-0.7637613775,2.8116565568
H,-2.6793764798,0.9860954618,-2.2795891362
H,2.7789171519,0.5732395916,1.2481453948
H,1.5991165479,1.1059005362,-1.0824607052
H,-1.2492959513,-0.1853800639,1.639916404
H,-2.0404851741,-0.6107673371,-2.9685069815
H,-0.641993314,-1.7031405547,0.9855052963

Frequencies

126.2571	159.9804	255.0551
402.6299	504.5245	532.4125
560.4703	562.9396	643.8976
749.8079	813.4930	833.1330
883.9635	921.3392	943.2518
960.1862	1004.6080	1050.6612
1107.7196	1140.1223	1191.9770
1207.2545	1285.2992	1333.7021
1396.2106	1448.1903	1470.3408
1508.8949	1961.4620	3031.9543
3059.6931	3095.1276	3158.9865
3210.1624	3233.7627	3244.0804

Rotational constants (GHZ): 7.85657 1.79680 1.49076

Well 5



C,-1.1546248859,1.1846559302,-0.0238240514
C,0.2447829453,1.153365704,-0.0186792624
C,0.9505605821,-0.0660700814,0.0135292595
C,0.1494829221,-1.195175863,0.0387881023
C,-1.2261065286,-1.2363931886,0.035518762
C,-1.8958604454,0.0006792201,0.0030038874
C,2.4602605077,-0.126184807,0.0196096687
H,-1.7776989405,-2.1721576307,0.0568196702
H,-2.9822663385,0.0291213058,-0.0010804376
H,-1.6671451057,2.1419505783,-0.0489696091
H,2.8305896355,-0.6373750533,0.9148559052
H,0.8059862014,2.0855707768,-0.0398588374
H,2.8360254686,-0.6783830426,-0.8486434031
H,2.8924429819,0.8781911514,-0.0024496542

Frequencies

42.5649	202.6650	328.9248
416.5368	484.1921	515.7008
630.4396	674.0440	740.9597
793.5211	846.3587	933.7262
979.3916	982.5915	1000.5686
1046.1645	1057.1247	1133.7982
1176.3705	1221.8613	1277.3611
1336.8909	1416.9678	1444.1454
1478.9520	1487.5928	1502.0119
1580.8498	1641.5900	3041.9794
3100.8928	3122.7112	3164.0071
3178.2354	3191.2781	3202.3188

Rotational constants (GHZ): 5.90916 2.48531 1.76870

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Transition States

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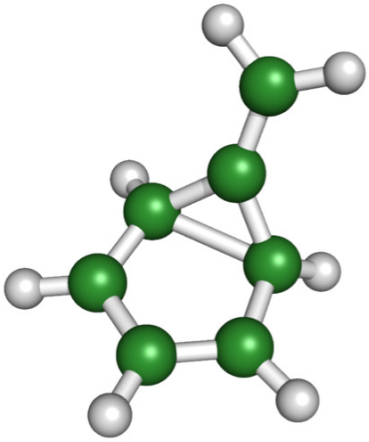
TS1



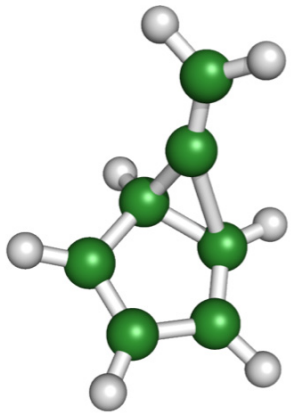
C,0.9737416235,-0.5476967217,0.0911159211
C,0.1591635261,-0.283067045,-1.0707732478
C,-0.9597789681,-0.5776787731,-0.1562465191
C,-1.2893776918,0.2735701297,0.9361625561
C,-0.2049070083,0.9407319615,1.5749952961
C,1.0121464937,0.451642951,1.1738255421
C,0.3010393785,-0.1930124358,-2.3934131743
H,-2.3044643452,0.3064701998,1.3222253576
H,-0.3340921329,1.7092406865,2.3283970675
H,1.963691653,0.7577224268,1.599753416
H,-1.604658383,-1.41718266,-0.4115313178
H,1.6053769885,-1.4346431227,0.1248920331
H,1.285885592,-0.1300998625,-2.8473776855
H,-0.5639034941,-0.1784480672,-3.0503571162

Frequencies

-692.1404	162.8295	279.0890
378.4993	470.8409	531.3585
588.9945	681.2563	699.6898
723.3619	767.6022	801.7855
856.0250	875.4117	894.2966
928.8028	962.5448	1028.0395
1052.0970	1111.6540	1122.4846
1191.1394	1274.2433	1312.0098
1355.6092	1411.2267	1459.9844
1527.6339	1761.6855	3149.3023
3153.5538	3155.8713	3191.1946
3193.8708	3226.4963	3238.1496

Rotational constants (GHZ): 5.66266 2.53153 1.99528

TS2



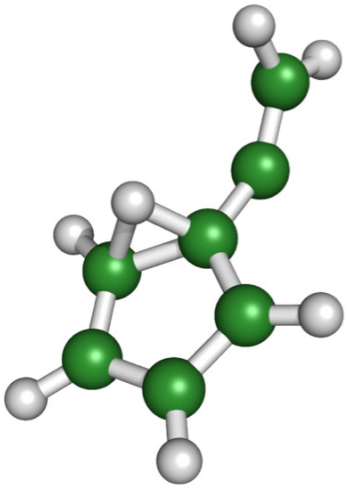
c,	-0.215399,	0.345579,	0.797200
c,	0.309416,	-1.050746,	0.497657
c,	1.457637,	-0.940483,	-0.275341
c,	1.740346,	0.456901,	-0.493138
c,	0.793614,	1.230507,	0.110278
c,	-1.298315,	-0.072750,	-0.088088
c,	-2.548266,	0.006691,	-0.489371
h,	2.019993,	-1.767065,	-0.692477
h,	-2.981374,	-0.698693,	-1.196841
h,	2.567745,	0.829901,	-1.087317
h,	0.717342,	2.310405,	0.085125
h,	-0.108836,	-1.949080,	0.931128
h,	-3.207968,	0.812746,	-0.146704
h,	-0.480370,	0.612074,	1.829684

Frequencies

-508.1518	121.2052	199.5925
302.3238	391.1513	534.88
584.7638	711.7284	741.3155
783.165	815.1317	846.5993
881.9396	913.6166	939.6871
947.8511	991.9554	1016.2312
1044.4454	1104.6961	1110.0765
1161.5817	1245.7384	1302.8704
1386.9505	1417.7744	1435.7974
1560.2955	1752.9793	3023.2456
3045.1804	3159.4185	3212.322
3231.5304	3243.9226	3258.1116

Rotational Constants (GHz): 5.90782 2.24596 1.93844

TS3



C,0.2977278643,-0.0500376468,-0.0261079042
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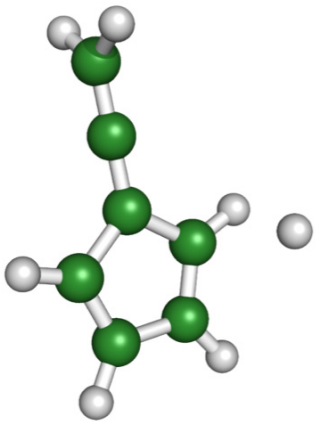
C,-1.9098244844,0.6899908336,0.2080094433
C,-1.9140634992,-0.6873752368,-0.1300299818
C,-0.6147644492,-1.1441674004,-0.2786057331
C,1.669022703,0.0147794176,-0.3988343939
C,2.903998068,-0.0001889941,0.0519916395
H,-2.7787473006,1.2940812366,0.4354759084
H,3.7624653375,0.1232132602,-0.6058565821
H,-2.8033221723,-1.3027250643,-0.2049567058
H,-0.2963738233,-2.1493697254,-0.5198911388
H,-0.2030870125,2.1332125696,0.4154672398
H,3.1292587003,-0.14770584,1.1146398902
H,0.1061315867,0.3239748151,1.1744048384

Frequencies

-1262.6336	105.7267	153.0810
315.6802	371.3125	567.4682
578.7101	597.4925	673.6854
766.1490	774.9956	842.6001
888.6029	901.3324	907.4978
942.1082	1006.9992	1069.4338
1084.3630	1089.9102	1164.4094
1198.4103	1244.4029	1306.2769
1430.3279	1446.3356	1468.5964
1523.5757	1784.4255	1998.5250
3052.3856	3169.6198	3221.0670
3240.8065	3254.6258	3261.1288

Rotational constants (GHZ): 7.99446 1.82637 1.52702

TS4



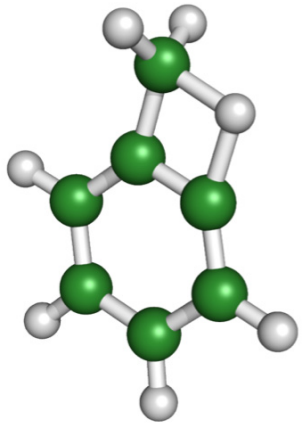
C,-0.1838245945,0.0620288229,-0.2284753191
C,-0.4151973322,-0.3664990115,1.1664540818
C,0.7696911587,-0.2444417463,1.8304156256
C,1.7968034628,0.233196572,0.9038315961
C,1.2431785879,0.4198681845,-0.3249131826
C,-1.0823607014,0.1164029179,-1.1989266762
C,-1.9675564108,0.1691630955,-2.1548906813
H,0.9374377057,-0.4701172663,2.8767696072
H,-2.5572849881,1.0665744113,-2.3319807047
H,2.8334498195,0.4059692736,1.1678851158
H,1.7261263568,0.7625846383,-1.2300033887
H,-1.3782716326,-0.6514642368,1.5658677823
H,-2.1462836246,-0.6839260908,-2.8067520623
H,-0.3795786597,-2.7679337403,0.7972409845

Frequencies

-153.0790	124.3430	142.9504
158.7142	167.7359	373.5899
482.0581	553.6534	563.3256
629.3486	644.2129	745.0943
773.5471	817.4623	871.8592
898.7117	919.7506	935.8919
996.0545	1014.0964	1095.4174
1103.9290	1186.3129	1286.7942
1316.8730	1400.7430	1467.4168
1512.3810	1595.3969	2026.5586
3132.2547	3207.3216	3221.9000
3234.2175	3257.4075	3264.8722

Rotational Constants (GHz): 7.19992 1.83874 1.52747

TS5



C,-1.3423856497,1.0545510267,0.024296466
C,0.0344245559,1.3325098674,0.0425534546
C,0.8908157254,0.2342321991,0.011200014
C,0.3941810499,-1.0549489843,-0.0358837038
C,-0.9584337433,-1.3681959492,-0.0548800462
C,-1.8279749872,-0.2615799664,-0.022972173
C,2.3573416337,-0.0912561128,0.0093779482
H,-1.3383339009,-2.3839877877,-0.0917914466
H,-2.9020884299,-0.4296735247,-0.0354079967
H,-2.0531879851,1.8759840615,0.047319302
H,1.7894920986,-1.3979650131,-0.0383175777
H,0.3946867084,2.3569926678,0.0796433241
H,2.9315353616,0.0830769747,-0.9022087538
H,2.9212755625,0.0224855409,0.9367641888

Frequencies

-2245.1718	187.4859	367.3728
392.0067	418.5640	489.0135
555.9417	633.0113	695.5235
745.8380	825.2740	875.8099
940.9717	967.9940	991.3614
996.9528	1025.1809	1049.6256
1121.9695	1134.2397	1177.2982
1210.2357	1278.1997	1345.7703
1429.7503	1463.4062	1487.5861
1596.2948	1647.2223	1798.1231
3088.3883	3172.9686	3181.6685
3184.6464	3198.7587	3208.8429

Rotational constants (GHZ): 5.56258 2.69405 1.83753

C_7H_5 Potential Energy Surface

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Wells
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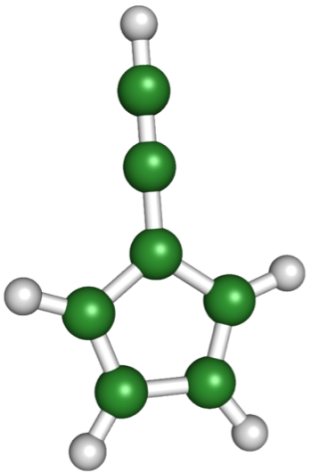
Well 1 Fulvenallenyl (C_7H_5)



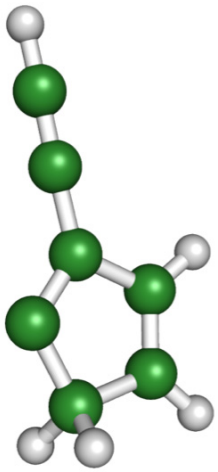
C,-0.277640165,-0.1292620176,0.11440285
C,0.9767353878,-0.0211038049,0.8412279402
C,1.8797734175,0.575941287,0.0060434085
C,1.2160558549,0.8633831181,-1.2810696654
C,-0.0812476772,0.437601222,-1.2100837183
C,-1.4620995906,-0.6800148018,0.6021723169
C,-2.4998191016,-1.162181216,1.0294876357
H,2.9130922739,0.8067928313,0.2349266857
H,-3.4058040167,-1.583301969,1.4025618142
H,1.6928965587,1.3352771952,-2.1315996161
H,-0.8433382485,0.4956924754,-1.9748756762
H,1.132604678,-0.360643253,1.8559021862

Frequencies

151.3625	165.4227	431.7683
519.2555	521.6416	560.9217
580.0979	628.8047	634.4905
647.2787	721.5564	753.0862
895.6889	909.6735	910.5508
996.2393	1044.0061	1092.9742
1123.6717	1288.7372	1302.9471
1411.9229	1506.6426	1530.9058
2096.5983	3226.0404	3237.1458
3259.1127	3262.9662	3474.4286

Rotational constants (GHZ): 8.45830 1.95771 1.58976

Well 2



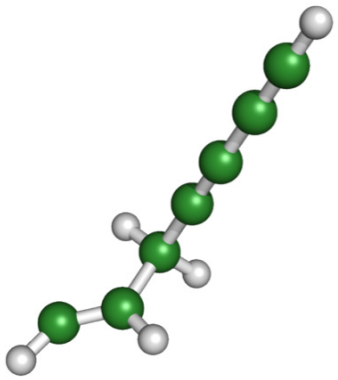
C,1.9034871394,-0.7428215069,0.0137857172
C,1.7786357043,0.7698355282,-0.0014438924
C,0.4764499383,1.1218188109,-0.0090551239
C,-0.3859603939,-0.0977647866,-0.0001654647
C,0.4668420746,-1.1434657002,0.0130666894
C,-1.8057348408,-0.0872400252,-0.0052934108
C,-3.0172118897,-0.0403842006,-0.0105820702
H,2.4437371163,-1.1255462893,-0.8629446601
H,2.6304578459,1.439906798,-0.0051872979
H,0.0714490557,2.1277065847,-0.020233199
H,2.4382330614,-1.1084020504,0.9011325099
H,-4.0829234718,-0.0135337603,-0.0146420204

Frequencies

143.7818	167.9228	317.8004
425.2047	521.0284	547.5815
593.5116	607.1137	661.0459
714.0339	798.5479	894.5853
896.2277	936.0788	937.5227
1025.4730	1105.4296	1118.4551
1182.8176	1247.2555	1330.5219
1420.0216	1564.0616	1643.8446
2212.0985	3039.7665	3070.1680
3215.0888	3237.3046	3482.6675

Rotational constants (GHZ): 9.11285 1.84324 1.54787

Well 3



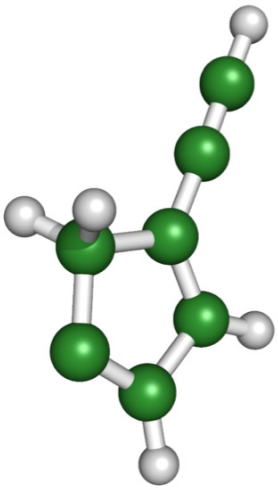
C,-1.4948016887,-0.7140108212,-0.2675638133
C,-2.2632117814,0.5045315274,0.2294758389
C,-3.1284382442,1.1836556588,-0.4869410649
C,1.1548109218,-0.419229289,-0.0008434048
C,-0.0473371021,-0.5606565427,-0.1281606875
C,2.5074349073,-0.2657553163,0.1400887772
C,3.7086236522,-0.1302367974,0.2649293144
H,-1.8153076619,-1.59732419,0.3036080079
H,-2.0556753338,0.8025122183,1.2639812418
H,-3.7805368064,2.0381796961,-0.3683323574
H,-1.7507253263,-0.905403906,-1.3158032474
H,4.7623644634,-0.0112032379,0.3734783952

Frequencies

64.6690	110.7087	162.4217
247.4367	339.3209	384.3617
451.9074	612.2274	616.4487
624.9816	721.8593	728.3245
748.3567	784.8156	820.2635
922.8041	1046.4238	1173.1334
1201.1419	1264.5801	1325.1301
1461.8187	1679.7079	2165.0080
2343.6973	3018.7510	3062.3753
3079.1653	3268.7756	3482.4908

Rotational constants (GHZ): 13.41759 0.95495 0.91254

Well 4



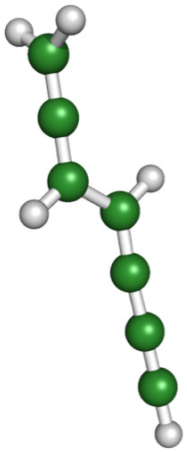
C,-1.9658288878,-0.6359809881,-0.0027201984
C,-0.5722963061,-1.1147114198,-0.008703619
C,0.2931425693,-0.0597571611,-0.0005630481
C,-0.51707194,1.2407140839,0.0119184679
C,-1.9078665915,0.7028541212,0.0092956963
C,1.7052301267,-0.089707896,-0.0023330425
C,2.9204715112,-0.0756843616,-0.0068457081
H,-0.2964886641,1.8452567626,0.9005343741
H,-2.8411432068,-1.2733418085,-0.0072931761
H,-0.2846479068,-2.1605812387,-0.0182746271
H,-0.2988488856,1.8604741167,-0.8666444595
H,3.9864457725,-0.0781661031,-0.0086134

Frequencies

153.5997	170.3110	311.4130
449.0531	519.8249	525.4601
552.2465	579.9995	663.6834
794.2524	809.5112	854.1579
897.1077	904.3508	985.5058
1004.0033	1110.6687	1162.8292
1231.9009	1249.5027	1289.6635
1419.2493	1539.4294	1630.4718
2188.6263	3056.0606	3092.8566
3218.0872	3241.2687	3481.9836

Rotational constants (GHZ): 8.54087 1.93264 1.59164

Well 5



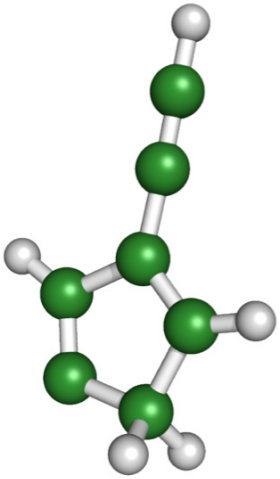
C,-1.9195238809,1.8413619367,0.0063305971
C,-1.7207024143,0.5500168212,-0.0036655334
C,-1.5236830127,-0.7554241781,-0.0138068397
C,-0.1959372904,-1.3736617906,-0.0107752052
C,0.0260174349,-2.678275867,-0.0207146927
C,0.3775845655,-3.9488567779,-0.0295457263
C,0.6892995704,-5.1503169412,-0.0380445456
H,-2.0121370285,2.3951000327,0.9390991546
H,-2.3859589611,-1.4203426375,-0.0250412731
H,0.6546766973,-0.6864120912,0.0005683692
H,-2.0004158722,2.4112713465,-0.9177483492
H,0.9509551922,-6.1834328536,-0.0453829556

Frequencies

47.0800	70.5881	174.3582
240.2230	293.6831	357.8761
388.8960	462.4889	522.8280
549.7718	575.5976	616.9635
831.4721	884.0379	907.4360
930.3798	1010.9915	1062.0741
1160.3592	1261.1230	1389.3583
1479.1512	1778.5702	1986.9648
2035.9107	3092.8977	3126.0436
3159.3409	3199.1210	3473.4909

Rotational constants (GHZ): 36.23029 0.87515 0.85956

Well 6



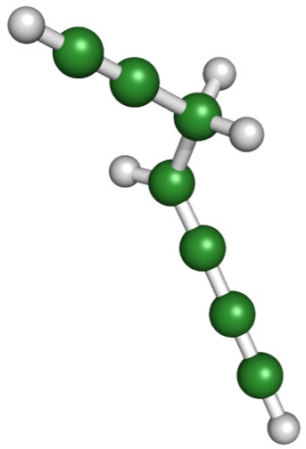
C,-1.7588963288,0.897669026,0.0158764405
C,-0.4716310946,1.2500795615,0.0101484763
C,0.3096100057,-0.0265563284,0.004219078
C,-0.5488920936,-1.0827347564,0.0068864714
C,-1.9781436826,-0.5801169276,0.0150500881
C,1.7300734157,-0.0765511979,-0.0032374355
C,2.9432360462,-0.0820628726,-0.0095694666
H,-2.5416409647,-0.9213304893,-0.8642112966
H,-2.5317691825,-0.923789997,0.899613959
H,-0.0272246751,2.2367491078,0.0092798309
H,-0.272847481,-2.1303508512,0.0040867411
H,4.0092300354,-0.0994912749,-0.0152838866

Frequencies

159.4244	169.7415	306.6043
410.5578	527.1399	544.6439
611.7623	635.7840	659.5971
742.2901	800.5684	822.2556
890.3165	911.7782	960.6107
967.9941	1106.8997	1139.5913
1221.6313	1257.2589	1280.1748
1420.5818	1568.1257	1636.8630
2204.1344	3039.5338	3069.7315
3235.1140	3249.4143	3481.6099

Rotational constants (GHZ): 8.50160 1.92669 1.58618

Well 7



C,3.3194323589,-0.7797611936,0.0489060014
C,2.3454742323,-0.1009348318,-0.1853844627
C,1.1592328771,0.7174291604,-0.4478703932
C,0.0543689297,0.4846002803,0.57957036
C,-1.182842165,0.1647515617,0.2818654807
C,-2.4384603725,-0.1575809125,0.021269669
C,-3.6135886708,-0.4594440684,-0.2295869611
H,0.7770961617,0.5150918452,-1.4539195983
H,1.4449473309,1.7790045949,-0.4230720411
H,4.1783276019,-1.3792676624,0.2478968181
H,0.3544943899,0.6034763923,1.6240756453
H,-4.6252826741,-0.720862166,-0.4403945183

Frequencies

41.6773	62.6453	181.5345
242.4976	299.6548	339.0324
392.1575	469.0877	487.1202
589.5586	624.6686	628.8373
646.9576	724.2356	866.8584
951.7673	969.5489	1056.4749
1204.7513	1289.5111	1348.1704
1464.9359	1812.1812	2020.4935
2221.6138	3019.6781	3084.5500
3101.7035	3472.0269	3482.0188

Rotational constants (GHZ): 12.78941 0.98159 0.95890

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Transition States

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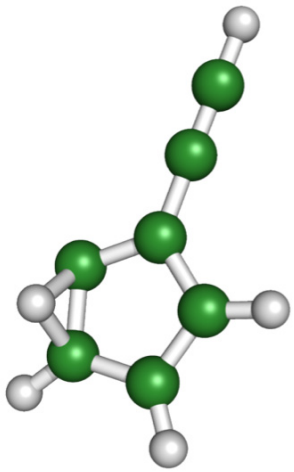
TS 1



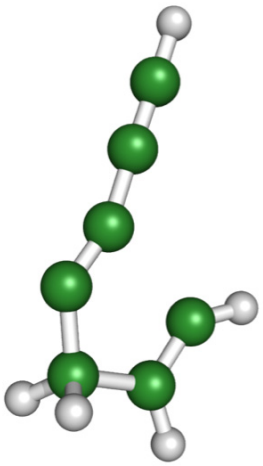
C,1.9319474628,0.5846849135,0.0095976306
C,1.2777757354,0.82490512,-1.2401594608
C,-0.0387237217,0.3775962285,-1.1443259185
C,-0.295957189,-0.177823833,0.1450100817
C,0.910821132,-0.0319882025,0.8541441795
C,-1.5148797988,-0.7274510545,0.6145814982
C,-2.5619911232,-1.2011390412,1.0030908514
H,2.9860465239,0.6425500404,0.2465298201
H,1.7155862798,1.358521809,-2.0741911343
H,-0.7986568934,0.4786550159,-1.9109280802
H,1.3226403976,1.2477995463,0.9397612724
H,-3.4795712933,-1.6202311966,1.3471949494

Frequencies

-1390.1298	157.4827	171.9513
449.6127	529.5710	549.8323
567.4704	571.5704	624.9126
670.9566	723.9340	819.4934
840.1436	888.6847	923.2322
1056.6054	1064.8398	1136.7570
1174.2354	1254.4696	1322.9946
1376.9135	1436.2832	1510.7955
2085.0885	2208.4126	3222.1940
3241.1952	3257.2646	3483.8676

Rotational constants (GHZ): 9.44175 1.86387 1.56789

TS2



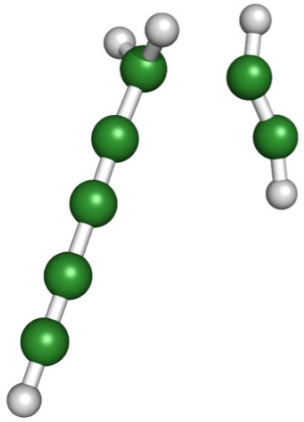
C,1.8724238145,-0.8131669995,0.0000790162
C,1.9461075164,0.7118774147,0.0000110041
C,0.8146041964,1.3898019228,-0.0000856664
C,-0.6240300328,-0.444914523,-0.0000264882
C,0.4302776525,-1.1201971787,0.0000347272
C,-1.9634015231,-0.140080518,-0.000069016
C,-3.1420902322,0.1584664531,0.0000331647
H,2.3775640428,-1.2364038948,-0.878439431
H,2.9264787196,1.1925138636,0.0000218037
H,0.4939636668,2.4227953615,-0.0001215268
H,2.3774763101,-1.2363000768,0.8786983094
H,-4.178831089,0.406675318,-0.0000196053

Frequencies

-485.2676	134.6167	139.1621
298.5449	330.2518	441.6268
496.5110	573.0321	603.8044
621.5113	640.9230	646.5542
746.9180	822.7823	837.7439
943.7347	950.8837	1138.7552
1177.2044	1202.3694	1296.8553
1458.9999	1654.3550	2006.7468
2216.3399	3035.2227	3060.6015
3126.2098	3265.7933	3481.8637

Rotational constants (GHZ): 7.51719 1.64930 1.36391

TS3



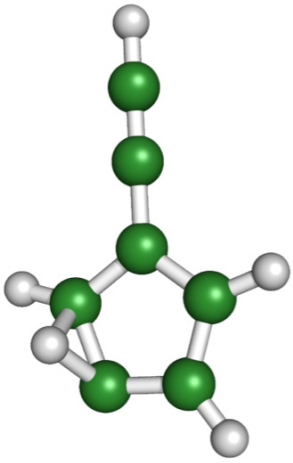
C,-1.3666574034,2.6033778747,-1.9758882544
C,-1.4045538023,1.5867765598,-1.2664002364
C,0.1354905194,0.1274090033,-1.6108004949
C,0.4204132985,-0.4537843924,-0.3807620499
C,0.6014637135,-0.9148021567,0.7475643136
C,0.8199673216,-1.4381572953,1.9813985015
C,1.0175890407,-1.9093672379,3.0888224061
H,0.8815480703,0.784383146,-2.0476140138
H,-1.9148034852,1.0546946848,-0.4856173092
H,-1.0502827446,3.3202776589,-2.7030226607
H,-0.4485808842,-0.4481890669,-2.3247216175
H,1.1898429162,-2.3198805563,4.0573704875

Frequencies

-601.8016	29.1219	74.1358
159.1628	199.6399	259.0756
342.8908	433.3059	529.7550
571.3352	581.1092	608.6895
660.2313	673.8538	700.2410
726.8849	772.3599	836.7030
937.3292	1056.5148	1264.5219
1461.0937	1840.6546	2113.0041
2188.8262	3140.3967	3224.3582
3349.7830	3447.0148	3480.5295

Rotational constants (GHZ): 10.08374 0.92266 0.86015

TS 4



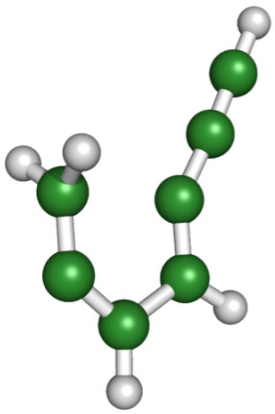
C,-1.9163201009,-0.6873475122,-0.0311221049
C,-0.5752875176,-1.1122047766,-0.0256452631
C,0.3029159049,-0.0049582175,-0.0667752624
C,-0.5012288198,1.1870023222,-0.0871488075
C,-1.8804703697,0.7134950825,-0.0383386475
C,1.7161971546,-0.0321776851,0.0166375867
C,2.9291622149,-0.0496359712,0.0798587451
H,-1.2174196257,1.2400160358,0.9978059189
H,-2.7957329865,-1.3144699917,0.0060894987
H,-0.2502376498,-2.1433663444,0.058107172
H,-0.180205082,2.2026027108,-0.274972109
H,3.9937845453,-0.0698218634,0.1281720407

Frequencies

-1400.7748	163.8942	171.9339
470.7694	534.0272	537.4592
558.1412	561.5067	611.7780
670.7256	706.1977	802.5655
826.6614	909.0081	934.4037
1028.6559	1079.2787	1172.5491
1204.1188	1240.2570	1311.3430
1361.1774	1404.7863	1501.5115
2086.0538	2191.6143	3222.2189
3260.0196	3262.6804	3482.3710

Rotational constants (GHZ): 8.76473 1.94542 1.60487

TS 5



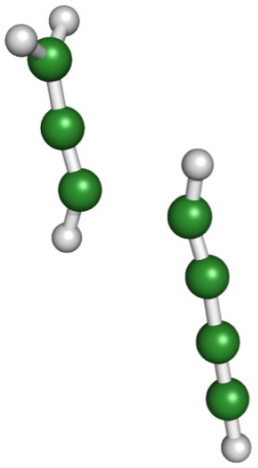
C,1.9361064296,-0.6323236157,0.0000810734
C,0.5692984866,-1.195320135,-0.0000286829
C,-0.463420235,-0.3416850953,-0.0001273425
C,0.8574134792,1.5655071554,0.0002280872
C,1.8971370016,0.6967137264,-0.0002737413
C,-1.8116803593,-0.2138948387,0.0000753015
C,-3.0223159761,0.0002076646,-0.0001569307
H,0.5359395761,2.0499091051,-0.9222246452
H,2.818900622,-1.26061737,-0.0007191253
H,0.4100038442,-2.2736810153,0.001106103
H,0.5360124303,2.048922093,0.9232286433
H,-4.0760894327,0.1602380171,-0.0001775645

Frequencies

-478.9511	128.2708	143.6443
266.0910	424.7883	433.7176
494.2878	508.2549	539.7716
557.3683	622.4673	715.7429
846.8259	849.0365	887.5624
919.1145	988.6390	1045.0219
1107.8870	1262.0429	1320.7314
1463.0704	1681.9243	1764.6150
2048.3008	3117.5459	3151.2636
3193.8041	3226.1843	3476.6611

Rotational constants (GHZ): 6.70672 1.80194 1.43417

TS 6



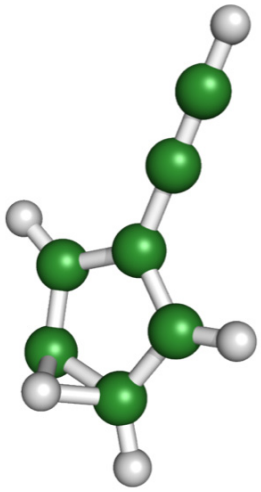
C,3.6621335455,0.0911136924,0.0184582821
C,2.4239462364,-0.4344109718,-0.0059463336
C,1.2238109256,-0.8082750322,-0.0263286074
C,-0.2356288642,0.9512165039,-0.021124413
C,-1.4196808438,0.6008137617,-0.0087282243
C,-2.6624008645,0.0515833722,0.0068846772
C,-3.7799440151,-0.4361177954,0.0224502366
H,4.1989884744,0.3059262932,-0.9011858118
H,0.5330790275,-1.6269502711,-0.0452546562
H,0.5602679236,1.6646154378,-0.0311928199
H,4.1723983653,0.2811710679,0.958463825
H,-4.7604739105,-0.8546910588,0.0357158455

Frequencies

-489.9679	16.0550	67.3945
117.1244	255.8951	287.3479
288.1916	377.6145	468.6698
520.9794	590.0000	603.9294
627.7346	647.4167	672.7796
692.0550	778.3386	798.1978
928.7429	1032.8495	1145.3526
1471.2748	1911.1494	2024.3829
2186.4382	3149.1674	3235.2819
3390.4610	3423.2829	3479.5391

Rotational constants (GHZ): 14.14975 0.85484 0.81072

TS 7



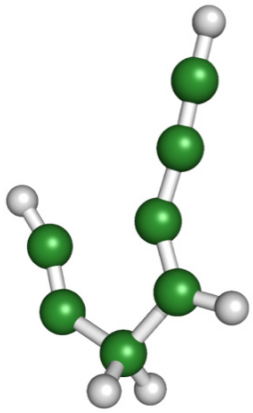
C,-1.833234974,0.8127042811,-0.1013178412
C,-0.5035937846,1.2203567227,-0.1223336498
C,0.2687914991,0.0213021471,-0.0823482022
C,-0.5802249694,-1.1037332475,-0.0597963197
C,-1.9291277096,-0.6504941862,-0.0750877764
C,1.6905341544,-0.0188299533,-0.0050362515
C,2.9013852501,-0.0465022157,0.0572607469
H,-2.8317075533,-1.2235394375,-0.239585294
H,-2.1513735876,0.0869996477,0.9795239898
H,-0.1179194614,2.2291368577,-0.1166224927
H,-0.2641267,-2.133072289,0.0479665187
H,3.9659638361,-0.0739043271,0.1066135722

Frequencies

-1418.7613	171.8467	172.8922
456.7943	536.3087	539.9067
560.5297	605.4406	648.9722
661.2847	709.8913	789.4677
819.6144	851.7547	933.2843
1016.7759	1067.3840	1145.0002
1198.1377	1246.7465	1343.5855
1366.6290	1394.8136	1507.9237
2051.5121	2207.6341	3243.1440
3260.3458	3271.0621	3482.0591

Rotational constants (GHZ): 8.72890 1.95652 1.61110

TS 8



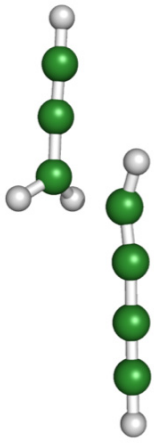
C,-1.7916456725,0.8178775126,0.000147533
C,-0.8084991638,1.5802157334,0.0000615229
C,0.4804726144,-0.300854446,-0.0001262039
C,-0.5176106028,-1.1791974307,-0.0000203556
C,-1.9461961617,-0.6496615065,0.0000081615
C,1.834434283,-0.1624317971,0.0000379577
C,3.0383803111,0.07434959,-0.0001438298
H,-2.4999804086,-1.0062703016,-0.8788160118
H,-2.5002541511,-1.0066559026,0.8784933953
H,-0.2671940984,2.5034401545,0.0000710635
H,-0.3409620322,-2.2546841892,0.0004928026
H,4.0894820826,0.2516505832,-0.0001890354

Frequencies

-503.5791	127.0299	152.3142
308.1597	325.5261	421.0076
486.3121	524.2373	541.0511
597.7995	661.9000	663.3413
753.5378	772.0740	871.4864
951.6445	994.2012	1013.1399
1175.1764	1232.9913	1308.2538
1459.4743	1737.5177	1943.7565
2069.5302	3035.3305	3060.1815
3153.0089	3422.9981	3476.9224

Rotational constants (GHZ): 6.64267 1.80268 1.43038

TS 9



C,3.6359599227,-0.1018554134,0.1973223437
C,2.5396767707,0.1047160981,-0.3041535945
C,1.2570013052,0.3188118006,-0.8067183894
C,-0.1552914071,-0.2027890104,0.9086621574
C,-1.3558499532,-0.1201798544,0.6171097641
C,-2.6184689677,0.0215638517,0.139340877
C,-3.7562961249,0.1448481523,-0.2838602465
H,0.8337751597,-0.4104173274,-1.489468736
H,0.8942489141,1.3371945134,-0.8992711737
H,4.6105549596,-0.2700983356,0.595170468
H,0.6416120932,-0.4062216973,1.594544542
H,-4.7537246722,0.2509302224,-0.6453220121

Frequencies

-491.0946	17.6970	69.2662
120.8513	262.2760	289.8736
355.8541	450.3133	510.5300
519.6824	523.3929	575.3133
606.6680	618.3546	644.2876
652.1181	733.5415	858.0456
930.7604	1051.7819	1056.0841
1461.3831	1987.0992	2090.1529
2170.1719	3159.5476	3250.5120
3395.5211	3476.3020	3478.8716

Rotational constants (GHZ): 14.21102 0.87589 0.82990