

Supporting Information

Unravelling the kinetics and molecular mechanism of the degenerate Cope rearrangement of bullvalene

Mahya Khojandi^a, Ahmad Seif^{a,†}, Ehsan Zahedi^b, Luis R. Domingo^c, Mehrnoosh Karimkhani^a

^a *Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran*

^b *Department of Chemistry, Shahrood Branch, Islamic Azad University, Shahrood, Iran*

^c *Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain*

† Corresponding author.

E-mail addresses: ahmaseif@yahoo.com

The optimized Cartesian coordinates at the QCISD-FC/6-311G(*d,p*) level of theory for bullvalene

C	1.08234900	-1.17444300	0.84387100
C	1.55510900	0.00000100	0.00000100
C	1.08234900	-0.14359200	-1.43903200
C	-0.21314800	-0.17938700	-1.79775600
C	-0.21314800	-1.46721100	1.05423100
C	-1.37603400	-0.71806400	0.51595000
C	-1.37603600	-0.08779400	-0.87983600
C	1.08234800	1.31803500	0.59516200
C	-0.21314900	1.64659700	0.74352400
C	-1.37603500	0.80585700	0.36388700
H	1.84318900	-1.80700000	1.29837600
H	2.65004000	0.00000200	0.00000200
H	1.84318800	-0.22093200	-2.21409600
H	-0.45739400	-0.28478600	-2.85402300
H	-0.45739400	-2.32926800	1.67363900
H	-2.33835100	-1.12835600	0.81075900
H	-2.33835100	-0.13795800	-1.38256500
H	1.84318700	2.02793100	0.91571400
H	-0.45739600	2.61405100	1.18037700
H	-2.33835100	1.26631300	0.57181000

The optimized Cartesian coordinates at the QCISD-FC/6-311G(*d,p*) level of theory for TS

C	-1.24936100	-0.57259300	-1.03411400
C	-1.51025800	0.48701600	0.00000100
C	-1.24936100	-0.57259700	1.03411200
C	-0.00000100	-0.98233700	1.50114200
C	-0.00000100	-0.98233200	-1.50114600
C	1.24936100	-0.57259400	-1.03411500
C	1.24936000	-0.57259800	1.03411400
C	-0.66893100	1.73351500	0.00000300
C	0.66893400	1.73351400	0.00000300
C	1.51025800	0.48701300	0.00000100
H	-2.12776400	-1.08985900	-1.41262800
H	-2.56843300	0.75749900	0.00000100
H	-2.12776500	-1.08986400	1.41262400
H	-0.00000200	-1.81884700	2.19809000
H	-0.00000100	-1.81883900	-2.19809700
H	2.12776300	-1.08985900	-1.41263200
H	2.12776300	-1.08986500	1.41262800
H	-1.20179500	2.68305300	0.00000200
H	1.20179900	2.68305100	0.00000300
H	2.56843400	0.75749500	0.00000200

Table S1. Unscaled harmonic vibrational frequencies and rotational moments of inertia calculated at the B3LYP/CBSB7 level of theory, as well as CBS energy

	Bullvalene			TS		
	234.2841,	234.4208,	280.5155,	297.5355i,	224.1048,	290.4814,
	364.4574,	364.4716,	453.9800,	293.1036,	348.9779,	428.9370,
	570.7333,	593.5521,	593.7839,	434.1306,	545.8573,	564.6110,
	665.0627,	665.1537,	756.4140,	639.0318,	677.9963,	701.0394,
	756.9061,	757.0600,	776.4508,	720.4314,	774.8002,	786.6388,
	841.2011,	841.2263,	844.7914,	819.5765,	845.8067,	863.7566,
	934.6927,	945.1354,	945.4591,	872.7022,	907.1339,	925.4358,
	979.1389,	984.8866,	984.9009,	947.4361,	960.5860,	976.0763,
Frequencies (cm ⁻¹)	1023.6079,	1023.8146,	1094.4228,	988.9956,	1003.4933,	1111.3187,
	1094.5328,	1117.1780,	1201.7867,	1165.3226,	1201.4586,	1204.1521,
	1234.8586,	1234.9126,	1266.3703,	1247.7419,	1250.0796,	1259.5643,
	1342.8481,	1343.1009,	1377.9531,	1277.3773,	1383.9019,	1386.7437,
	1378.0023,	1393.6278,	1431.6822,	1393.4750,	1410.0422,	1437.6789,
	1431.6957,	1436.0109,	1690.3051,	1472.0935,	1506.3347,	1512.5274,
	1698.3059,	1698.3859,	3067.7316,	1616.1702,	1738.9581,	3087.0301,
	3129.2970,	3129.3115,	3132.1488,	3088.3741,	3134.7475,	3135.2368,
	3149.0630,	3149.1367,	3159.0540,	3136.5497,	3159.0421,	3169.6637,
	3159.6221,	3159.6631,	3169.6842	3173.0463,	3174.9582,	3180.5989
I_a, I_b, I_c (amu. Bohr ²)	948.60479,	1094.99364,	1095.17999	956.51228,	1070.72057,	1124.83103
CBS-QB3 (a.u.)		-386.404452			-386.384580	

Table S2. Unscaled harmonic vibrational frequencies and rotational moments of inertia calculated at the HF/6-311G(*d,p*) level of theory, as well as CBS energy

	Bullvalene			TS		
	270.8005,	270.8346,	304.9118,	596.8281i,	254.2387,	324.9415,
	385.1118,	385.1372,	483.1542,	330.2670,	383.9308,	458.0983,
	619.1719,	653.7832,	653.8275,	458.3750,	603.2906,	618.9764,
	740.3491,	740.3580,	815.4654,	692.7445,	744.7131,	781.0401,
	817.9511,	817.9722,	834.5925,	802.3102,	833.5844,	849.1489,
	888.0859,	918.5269,	918.5286,	868.2677,	901.7981,	947.0919,
	1008.3677,	1038.9481,	1038.9729,	970.0893,	971.5200,	1002.9553,
	1102.4770,	1106.4760,	1106.4836,	1027.1582,	1059.2964,	1077.0396,
Frequencies (cm ⁻¹)	1122.0297,	1122.0461,	1169.3832,	1089.1382,	1108.7497,	1176.0676,
	1169.3986,	1239.9857,	1291.8207,	1242.5977,	1287.1382,	1299.1461,
	1325.8226,	1325.8314,	1355.7995,	1338.3306,	1338.7126,	1354.3347,
	1463.0921,	1463.1558,	1491.1026,	1378.3602,	1488.3042,	1502.1140,
	1491.1107,	1541.1615,	1550.3178,	1506.9888,	1541.9714,	1559.9434,
	1550.3224,	1558.2320,	1852.4996,	1589.0230,	1593.6451,	1643.4996,
	1855.8288,	1855.8460,	3216.2811,	1753.9797,	1893.1891,	3246.0843,
	3284.8382,	3284.8446,	3291.1433,	3247.7236,	3295.5877,	3296.6920,
	3299.1696,	3299.1826,	3312.8249,	3299.5601,	3321.9622,	3329.4809,
	3319.4524,	3319.4567,	3327.2077	3333.5952,	3336.8533,	3343.2272
<i>I</i> _a , <i>I</i> _b , <i>I</i> _c (amu. Bohr ²)	944.26542,	1085.97581,	1086.04277	943.50303,	1046.97407,	1119.53744
CBS-APNO (a.u.)		-386.983497			-386.963020	