Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Sp^2- and sp^3-C···O tetrel bonds in the 3-oxetanone homodimer

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Supporting Information:

Content:

Table S1. Experimental transition frequencies of the CE1.

J'	K_a'	K_c'	←	J''	K_a''	K_c''	ν_{obs}	$\Delta\nu_{obs-calc}$
5	0	5		4	0	4	7538.2407	-0.0003
5	1	5		4	1	4	7414.1104	0.0008
5	1	4		4	1	3	7718.1346	-0.0001
5	2	4		4	2	3	7570.1187	0.0009
5	2	3		4	2	2	7605.9064	-0.0016
5	3	3		4	3	2	7580.1765	0.0013
5	3	2		4	3	1	7580.8818	-0.0009
6	0	6		5	0	5	9026.8645	-0.0001
6	1	6		5	1	5	8892.2366	0.0002
6	1	5		5	1	4	9256.0453	0.0004
6	2	5		5	2	4	9080.6180	0.0026
6	2	4		5	2	3	9142.3662	-0.0029
6	3	4		5	3	3	9097.9939	0.0004
6	3	3		5	3	2	9099.8762	0.0003
7	0	7		6	0	6	10506.4429	-0.0004
7	1	7		6	1	6	10368.0870	0.0007
7	1	6		6	1	5	10790.5220	0.0002
7	2	6		6	2	5	10589.2017	0.0028
7	2	5		6	2	4	10685.8156	-0.0043
7	3	5		6	3	4	10616.5007	0.0008
7	3	4		6	3	3	10620.7177	-0.0026
7	4	4		6	4	3	10612.7616	0.0002
7	4	3		6	4	2	10612.8235	-0.0003
8	0	8		7	0	7	11976.9994	0.0005
8	1	8		7	1	7	11841.5000	0.0001
8	1	7		7	1	6	12320.7338	0.0004
8	2	7		7	2	6	12095.5684	0.0064
8	2	6		7	2	5	12235.8709	-0.0066
8	3	6		7	3	5	12135.5899	0.0008
8	3	5		7	3	4	12143.9807	-0.0022
9	0	9		8	0	8	13439.3679	-0.0004
9	1	9		8	1	8	13312.3989	-0.0002
9	1	8		8	1	7	13845.7441	0.0021
9	2	8		8	2	7	13599.4195	0.0088
9	2	7		8	2	6	13791.3166	-0.0109
9	3	7		8	3	6	13655.0751	0.0014
9	3	6		8	3	5	13670.3326	-0.0035
10	0	10		9	0	9	14895.0602	0.0006
10	1	10		9	1	9	14780.7836	-0.0012
10	1	9		9	1	8	15364.5167	0.0044
2	2	1		1	1	0	7605.8682	-0.0018
2	2	0		1	1	1	7668.6268	0.0012
3	2	2		2	1	1	9059.8126	0.0032

3	2	1	2	1	2	9251.6917	-0.0019
3	3	1	2	2	0	12221.3153	0.0013
3	3	0	2	2	1	12223.1587	-0.0025
4	3	2	4	2	3	7683.5381	-0.0028
4	3	1	4	2	2	7656.6852	0.0035
4	1	4	3	0	3	7294.6364	0.0001
4	2	3	3	1	2	10482.9764	-0.0004
4	2	2	3	1	3	10875.6968	0.0002
4	3	2	3	2	1	13732.5023	-0.0013
4	3	1	3	2	2	13741.7971	0.0006
4	4	1	3	3	0	16807.5414	0.0024
4	4	0	3	3	1	16807.5708	-0.0024
5	3	3	5	2	4	7693.5943	-0.0040
5	3	2	5	2	3	7631.6616	0.0052
5	1	5	4	0	4	8667.4454	0.0008
5	2	4	4	1	3	11875.5724	0.0000
5	2	3	4	1	4	12547.6561	-0.0034
5	3	3	4	2	2	15236.6219	0.0011
5	3	2	4	2	3	15264.6581	-0.0016
6	0	6	5	1	5	7897.6613	0.0003
6	1	6	5	0	5	10021.4395	-0.0005
6	2	5	5	1	4	13238.0551	0.0019
6	2	4	5	1	5	14275.9161	-0.0029
7	0	7	6	1	6	9511.8673	-0.0006
7	1	7	6	0	6	11362.6610	-0.0008
7	2	6	6	1	5	14571.2131	0.0060
8	0	8	7	1	7	11120.7802	-0.0002
8	1	8	7	0	7	12697.7184	0.0001
9	0	9	8	1	8	12718.6500	0.0012
9	1	9	8	0	8	14033.1162	-0.0024
10	0	10	9	1	9	14301.3084	-0.0009
10	1	10	9	0	9	15374.5338	-0.0013
2	2	1	1	1	1	7666.8129	0.0008
2	2	0	1	1	0	7607.6833	-0.0002
3	2	2	2	1	2	9242.6374	0.0006
3	2	1	2	1	1	9068.8611	-0.0051
3	3	1	2	2	1	12223.1266	-0.0009
3	3	0	2	2	0	12221.3476	-0.0001
4	3	1	4	2	3	7683.7756	-0.0014
4	3	2	4	2	2	7656.4449	-0.0007
4	1	3	3	0	3	7903.8373	-0.0006
4	2	3	3	1	3	10848.6028	0.0015
4	2	2	3	1	2	10510.0691	-0.0030
4	3	2	3	2	2	13741.5593	-0.0010
4	3	1	3	2	1	13732.7496	0.0099

4	4	1		3	3	1	16807.5708	-0.0019
4	4	0		3	3	0	16807.5404	0.0009
5	3	2		5	2	4	7694.5402	-0.0017
5	1	4		4	0	4	9580.6730	0.0017
5	2	4		4	1	4	12484.7783	0.0043
5	2	3		4	1	3	11938.4545	-0.0034
5	3	3		4	2	3	15263.7154	-0.0007
5	3	2		4	2	2	15237.5644	0.0000
6	1	5		5	0	5	11298.4772	0.0020
6	2	5		5	1	5	14151.2850	0.0051
6	2	4		5	1	4	13362.6864	-0.0059
6	3	4		5	2	4	16791.5904	-0.0014
6	3	3		5	2	3	16731.5346	0.0022
7	1	6		6	0	6	13062.1340	0.0016
8	1	7		7	0	7	14876.4231	0.0006

Table S2. Experimental transition frequencies of ^{18}O1 isotopologue of the CE1.

J'	K_a'	K_c'	←	J''	K_a''	K_c''	ν_{obs}	$\Delta\nu_{obs-calc}$
4	0	4		3	0	3	5948.2391	0.0010
5	0	5		4	0	4	7419.3270	0.0011
5	1	5		4	1	4	7288.9019	-0.0023
5	1	4		4	1	3	7616.5663	-0.0023
6	0	6		5	0	5	8880.6606	0.0009
6	1	6		5	1	5	8741.1511	-0.0029
6	1	5		5	1	4	9132.9742	-0.0032
7	0	7		6	0	6	10331.6296	-0.0005
7	1	7		6	1	6	10190.7607	-0.0019
7	1	6		6	1	5	10645.1930	-0.0059
8	0	8		7	0	7	11772.6266	0.0042
2	2	1		1	1	0	7403.3800	0.0030
2	2	0		1	1	1	7471.2808	0.0039
3	3	0		2	2	1	11897.3488	-0.0034
6	0	6		5	1	5	7828.8774	0.0116
2	2	1		1	1	1	7469.0984	0.0028
4	1	3		3	0	3	7787.3312	0.0016
5	1	4		4	0	4	9455.6584	-0.0033

Table S3. Experimental transition frequencies of ^{18}O12 isotopologue of the CE1.

J'	K_a'	K_c'	←	J''	K_a''	K_c''	ν_{obs}	$\Delta\nu_{obs-calc}$
4	0	4		3	0	3	5855.3346	0.0001
5	0	5		4	0	4	7308.0512	-0.0028
5	1	5		4	1	4	7192.7742	0.0005
5	1	4		4	1	3	7469.4806	0.0028
6	0	6		5	0	5	8753.7741	-0.0019
6	1	6		5	1	5	8627.3834	0.0004
6	1	5		5	1	4	8958.6692	0.0031
7	0	7		6	0	6	10191.7592	-0.0017
7	1	7		6	1	6	10060.0548	-0.0012
7	1	6		6	1	5	10445.0541	0.0028
2	2	1		1	1	0	7529.2967	0.0007
2	2	0		1	1	1	7586.2355	-0.0041
3	3	1		2	2	0	12104.9919	0.0038
5	1	5		4	0	4	8474.7612	0.0044
6	0	6		5	1	5	7587.0642	-0.0081
6	1	6		5	0	5	9794.0934	0.0007
2	2	1		1	1	1	7584.7394	-0.0034
2	2	0		1	1	0	7530.7928	-0.0051

Table S4. Experimental transition frequencies of the CC1.

J'	K_a'	K_c'	←	J''	K_a''	K_c''	ν_{obs}	$\Delta\nu_{obs-calc}$
6	0	6		5	0	5	7165.5380	0.0011
6	1	6		5	1	5	7019.4717	-0.0009
6	1	5		5	1	4	7365.9513	-0.0005
6	2	5		5	2	4	7196.2943	-0.0013
6	2	4		5	2	3	7231.6234	0.0010
6	3	4		5	3	3	7206.1975	0.0019
6	3	3		5	3	2	7206.8236	0.0001
6	4	3		5	4	2	7204.3917	0.0025
6	4	2		5	4	1	7204.3917	-0.0012
7	0	7		6	0	6	8344.8698	0.0009
7	1	7		6	1	6	8185.7867	0.0007
7	1	6		6	1	5	8589.3103	-0.0018
7	2	6		6	2	5	8393.0266	-0.0007
7	2	5		6	2	4	8449.0812	0.0010
7	3	5		6	3	4	8408.7496	0.0004
7	3	4		6	3	3	8410.1606	0.0007
7	4	4		6	4	3	8406.0686	-0.0010
7	4	3		6	4	2	8406.0831	0.0012
7	5	3		6	5	2	8404.6558	-0.0002
7	5	2		6	5	1	8404.6558	-0.0003
8	0	8		7	0	7	9517.8955	0.0004
8	1	8		7	1	7	9350.5875	0.0004
8	1	7		7	1	6	9810.5267	-0.0015
8	2	7		7	2	6	9588.5374	-0.0026
8	2	6		7	2	5	9671.5766	0.0009
8	3	6		7	3	5	9611.8557	-0.0006
8	3	5		7	3	4	9614.6704	-0.0016
8	4	5		7	4	4	9608.1818	-0.0019
8	4	4		7	4	3	9608.2159	-0.0016
8	5	4		7	5	3	9606.0667	-0.0007
8	5	3		7	5	2	9606.0667	-0.0008
9	0	9		8	0	8	10684.3162	0.0002
9	1	9		8	1	8	10513.7621	0.0012
9	1	8		8	1	7	11029.1788	-0.0004
9	2	8		8	2	7	10782.6613	-0.0032
9	2	7		8	2	6	10899.2236	0.0020
9	3	7		8	3	6	10815.4957	0.0004
9	3	6		8	3	5	10820.6429	0.0007
10	0	10		9	0	9	11844.1732	0.0020
10	1	10		9	1	9	11675.2268	-0.0004
10	1	9		9	1	8	12244.8004	-0.0002
10	2	9		9	2	8	11975.2312	-0.0043
10	2	8		9	2	7	12131.7899	0.0035

11	0	11	10	0	10	12997.8612	0.0008
11	1	11	10	1	10	12834.9406	-0.0006
11	1	10	10	1	9	13456.8817	0.0000
11	2	10	10	2	9	13166.0890	-0.0038
11	2	9	10	2	8	13368.6738	0.0022
12	0	12	11	0	11	14146.1086	-0.0002
12	1	12	11	1	11	13992.8915	-0.0014
12	1	11	11	1	10	14664.8680	-0.0004
12	2	11	11	2	10	14355.0778	-0.0052
12	2	10	11	2	9	14608.9485	0.0046
2	2	1	1	1	0	9758.7020	-0.0025
2	2	0	1	1	1	9817.5823	-0.0010
3	3	1	3	2	2	12312.5627	-0.0020
3	3	0	3	2	1	12307.4807	0.0000
3	3	1	2	2	0	15912.0544	-0.0011
3	3	0	2	2	1	15913.0847	-0.0016
3	2	2	2	1	1	10901.0087	-0.0022
3	2	1	2	1	2	11079.6787	-0.0042
4	2	3	3	1	2	12014.2294	0.0034
4	2	2	3	1	3	12376.6342	-0.0003
4	3	2	4	2	3	12315.3773	0.0020
4	3	1	4	2	2	12300.1838	0.0004
4	3	2	3	2	1	17110.1428	-0.0006
4	3	1	3	2	2	17115.3170	-0.0003
5	3	3	5	2	4	12321.0443	0.0013
5	3	2	5	2	3	12285.7958	0.0005
5	1	5	4	0	4	8037.5949	-0.0036
5	2	4	4	1	3	13098.4505	-0.0042
5	2	3	4	1	4	13712.5189	0.0083
6	1	6	5	0	5	9076.5932	-0.0002
6	2	5	6	1	6	8001.9749	-0.0015
6	2	5	5	1	4	14153.9213	-0.0007
6	3	4	6	2	5	12330.9443	0.0013
6	3	3	6	2	4	12260.9957	-0.0007
7	1	7	6	0	6	10096.8454	0.0030
7	2	6	7	1	7	8209.2187	0.0009
7	2	6	6	1	5	15181.0003	0.0028
7	3	5	7	2	6	12346.6668	0.0019
7	3	4	7	2	5	12222.0763	0.0002
8	1	8	7	0	7	11102.5603	-0.0003
8	3	6	8	2	7	12369.9838	0.0026
8	3	5	8	2	6	12165.1688	-0.0036
9	0	9	8	1	8	9099.6521	0.0015
9	1	9	8	0	8	12098.4266	0.0002
10	0	10	9	1	9	10430.0606	-0.0003

10	1	10		9	0	9	13089.3429	0.0054
11	1	11		10	0	10	14080.1080	0.0006

Table S5. Experimental transition frequencies of ^{18}O1 isotopologue of the CC1.

J'	K_a'	K_c'	←	J''	K_a''	K_c''	ν_{obs}	$\Delta\nu_{obs-calc}$
5	0	5		4	0	4	5947.4001	-0.0058
5	1	5		4	1	4	5813.2016	-0.0046
5	1	4		4	1	3	6118.2319	0.0003
6	0	6		5	0	5	7124.1593	-0.0030
6	1	6		5	1	5	6972.7624	-0.0053
6	1	5		5	1	4	7338.3448	-0.0043
7	0	7		6	0	6	8294.3829	-0.0067
7	1	7		6	1	6	8130.7681	-0.0015
7	1	6		6	1	5	8556.3982	-0.0009
8	0	8		7	0	7	9457.4926	0.0005
8	1	8		7	1	7	9287.0592	0.0005
8	1	7		7	1	6	9771.9380	0.0004
9	0	9		8	0	8	10613.2762	0.0036
9	1	9		8	1	8	10441.5172	0.0018
9	1	8		8	1	7	10984.4599	0.0061
10	0	10		9	0	9	11761.9485	0.0080
2	2	1		1	1	0	9463.5526	-0.0020
2	2	0		1	1	1	9525.8050	-0.0017
3	3	1		2	2	0	15424.7432	0.0013
3	3	0		2	2	1	15425.9383	0.0009
6	1	6		5	0	5	8916.4413	-0.0006

Table S6. Experimental transition frequencies of ^{18}O12 isotopologue of the CC1.

J'	K_a'	K_c'	←	J''	K_a''	K_c''	ν_{obs}	$\Delta\nu_{obs-calc}$
5	0	5		4	0	4	5966.2182	0.0001
5	1	5		4	1	4	5834.4924	0.0028
5	1	4		4	1	3	6132.2346	-0.0048
6	0	6		5	0	5	7147.5344	0.0033
6	1	6		5	1	5	6998.4987	0.0057
6	1	5		5	1	4	7355.3807	-0.0003
7	0	7		6	0	6	8322.6929	-0.0004
7	1	7		6	1	6	8161.0395	0.0026
7	1	6		6	1	5	8576.6079	-0.0008
8	0	8		7	0	7	9491.1123	0.0026
8	1	8		7	1	7	9321.9603	0.0033
8	1	7		7	1	6	9795.4970	-0.0052
9	0	9		8	0	8	10652.5347	-0.0013
2	2	1		1	1	0	9601.5690	0.0024
5	1	5		4	0	4	7962.1982	0.0010
6	1	6		5	0	5	8994.4787	-0.0022
7	1	7		6	0	6	10007.9837	-0.0061

Table S7. Relative intensities (in arbitrary units) of selected μ_a-type transitions of isomers CE1 and CC1.

Transitions	Conformer	Frequencies	Intensities
$6_{06} \leftarrow 5_{05}$	CE1	9026.8645	0.0226
	CC1	7165.5380	0.0101
$6_{16} \leftarrow 5_{15}$	CE1	8892.2366	0.0161
	CC1	7019.4717	0.0087
$6_{15} \leftarrow 5_{14}$	CE1	9256.0453	0.0179
	CC1	7365.9513	0.0112
$7_{07} \leftarrow 6_{06}$	CE1	10506.4429	0.0152
	CC1	8344.8698	0.0100
$7_{17} \leftarrow 6_{16}$	CE1	10368.0870	0.0131
	CC1	8185.7867	0.0095
$7_{16} \leftarrow 6_{15}$	CE1	10790.5220	0.0102
	CC1	8589.3103	0.0081
$7_{26} \leftarrow 6_{25}$	CE1	10589.2017	0.0098
	CC1	8393.0266	0.0054
$7_{25} \leftarrow 6_{24}$	CE1	10685.8156	0.0103
	CC1	8449.0812	0.0068
$8_{08} \leftarrow 7_{07}$	CE1	11976.9994	0.0082
	CC1	9517.8955	0.0096
$8_{18} \leftarrow 7_{17}$	CE1	11841.5000	0.0073
	CC1	9350.5875	0.0085
$8_{17} \leftarrow 7_{16}$	CE1	12320.7338	0.0086
	CC1	9810.5267	0.0094

Table S8. Stabilization energy contributions to the CE1 from NBO results.

Donor NBO	Acceptor NBO	E(2) kJ/mol
From 3OXT unit 1 to 3OXT unit 2		
BD(1)C12-O10	RY*(3)C2	0.29
BD(1)C12-O10	RY*(5)C2	0.29
BD(1)C14-H15	BD*(1)C5-H9	0.21
BD(1)C14-O10	RY*(5)C5	0.33
BD(2)C11-O12	RY*(1)9	0.63
LP(1)O10	RY*(1)H7	0.25
LP(1)O10	BD*(1)C4-H7	0.88
LP(1)O10	BD*(1)C4-H6	0.67
LP(1)O10	BD*(2)C2-O1	1.63
LP(2)O10	RY*(1)C5	0.42
LP(2)O10	RY*(5)C5	0.38
LP(2)O10	RY*(2)H9	0.33
LP(2)O10	RY*(1)C2	0.50
LP(2)O10	RY*(4)O3	0.21
LP(2)O10	BD*(1)C10-H6	0.54
LP(2)O10	BD*(1)C10-O3	0.21
LP(2)O10	BD*(1)C11-H8	0.46
LP(2)O10	BD*(1)C2-O1	0.21
LP(2)O10	BD*(2)C2-O1	5.73
From 3OXT unit 2 to 3OXT unit 1		
BD(1)C4-C2	RY*(1)O10	0.25
BD(1)C4-C2	RY*(2)O10	0.33
BD(1)C4-O3	RY*(1)H15	0.25
BD(1)C5-H9	BD*(2)C11-O12	0.25
BD(1)C5-H8	RY*(4)O10	0.42
BD(1)C5-O3	RY*(1)H15	0.33
BD(2)C2-O1	BD*(1)C13-H17	0.33
LP(2)O1	BD*(1)C13-H17	0.29
LP(1)O3	BD*(1)C14-H15	0.71
LP(2)O3	RY*(1)H15	0.33
LP(2)O3	RY*(2)H15	0.38
LP(2)O3	RY*(5)O10	0.25
LP(2)O3	BD*(1)C14-H15	1.97

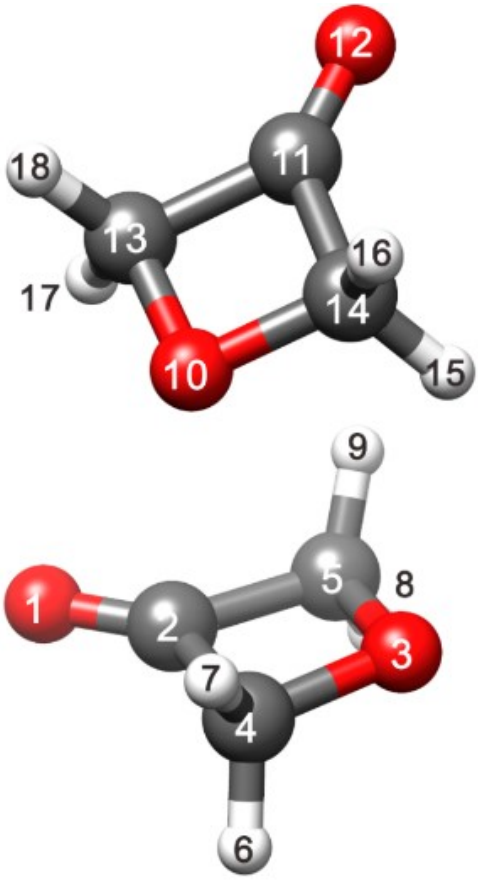

Table S9. Stabilization energy contributions to the CC1 from NBO results.

Donor NBO	Acceptor NBO	E(2) kJ/mol
From 3OXT unit 1 to 3OXT unit 2		
BD(1)C14-C11	RY*(1)C2	0.33
BD(1)C14-C11	RY*(5)C2	0.33
BD(1)C13-H15	BD*(2)C2-O1	0.25
BD(1)C13-H16	BD*(2)C2-O1	0.25
BD(1)C11-O10	RY*(1)C2	0.33
LP(1)O10	BD*(2)C2-O1	1.63
LP(2)O10	BD*(1)C2-O1	0.38
LP(2)O10	BD*(2)C2-O1	5.23
From 3OXT unit 2 to 3OXT unit 1		
BD(1)C2-O1	RY*(1)C11	0.25
BD(1)C2-O1	RY*(5)C11	0.46
BD(2)C2-O1	RY*(5)C13	0.63
BD(2)C2-O1	BD*(1)C13-O12	1.59
LP(1)O2	BD*(1)C13-O12	1.09
LP(2)O3	RY*(2)O10	0.67

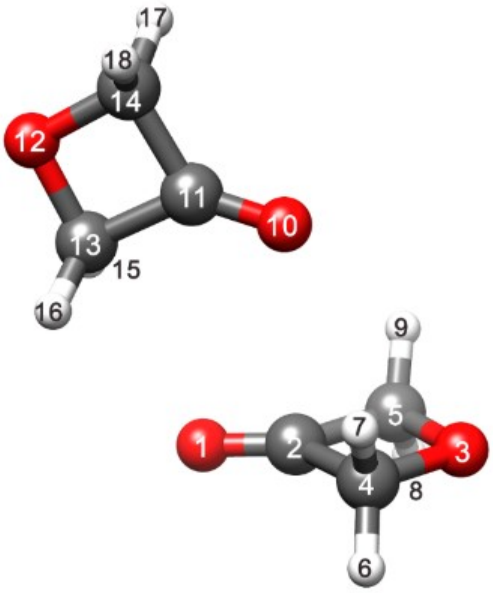

Table S10. Coordinates of isomer CE1 and CC1 calculated at the B2PLYP-D3(BJ)/6-311++g(d,p) level of theory.

	CE1			CC1		
	a [Å]	*b* [Å]	*c* [Å]	*a* [Å]	*b* [Å]	*c* [Å]
O1	1.8734	1.7702	0.2942	0.9314	1.6595	-0.0015
C2	1.8536	0.5740	0.2492	-1.6767	0.7195	-0.0006
O3	1.6921	-1.5110	0.1421	-3.0491	-0.8604	0.0011
C4	2.2376	-0.5068	-0.7597	-2.3788	-0.1277	1.0573
C5	1.4148	-0.5502	1.1893	-2.3798	-0.1291	-1.0567
H6	3.3150	-0.6281	-0.9053	-3.0765	0.4112	1.7042
H7	1.7091	-0.4618	-1.7114	-1.7084	-0.7590	1.6446
H8	2.0634	-0.6832	2.0608	-3.0780	0.4089	-1.7037
H9	0.3678	-0.5445	1.5027	-1.7099	-0.7612	-1.6437
O10	-0.6661	0.2561	-1.1068	0.5186	-1.1809	-0.0005
C11	-2.3038	-0.0329	0.1653	1.5469	-0.5620	-0.0001
O12	-3.1975	-0.2067	0.9418	3.3506	0.4981	0.0006
C13	-1.4892	1.1651	-0.3288	1.9578	0.9097	0.0010
C14	-1.4538	-0.9133	-0.7533	3.0322	-0.9135	-0.0006
H15	-0.8489	-1.6889	-0.2772	1.6786	1.4721	-0.8922
H16	-1.9980	-1.3229	-1.6090	1.6788	1.4708	0.8951
H17	-0.9140	1.7113	0.4230	3.3853	-1.4282	-0.8987
H18	-2.0492	1.8632	-0.9571	3.3856	-1.4298	0.8964

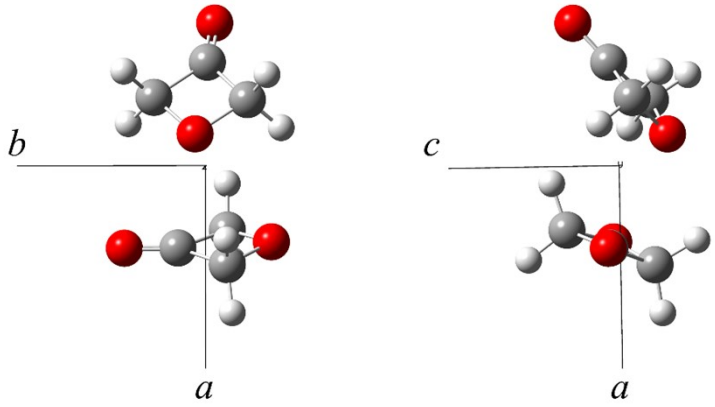

Figure S1 Geometries of two different perspectives of CE1.

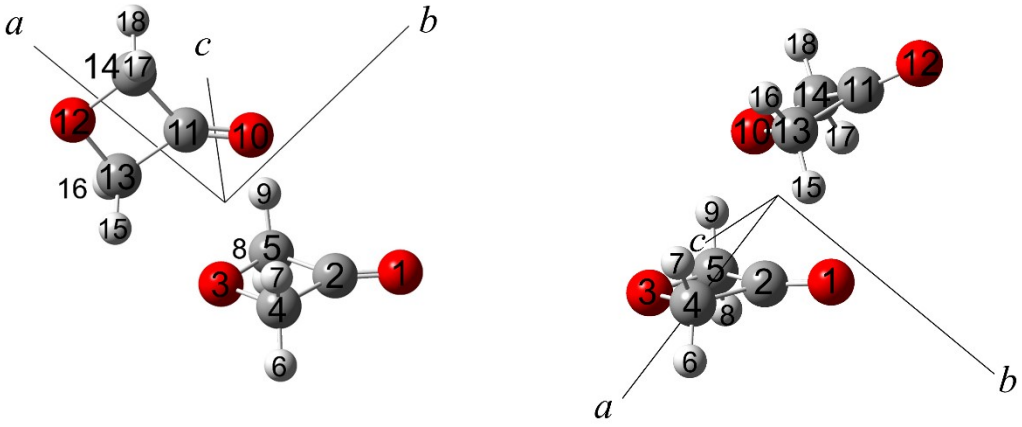

Figure S2 Shape, principal inertial axes and atom numbering of the CE3 (left) and CE2 (right).

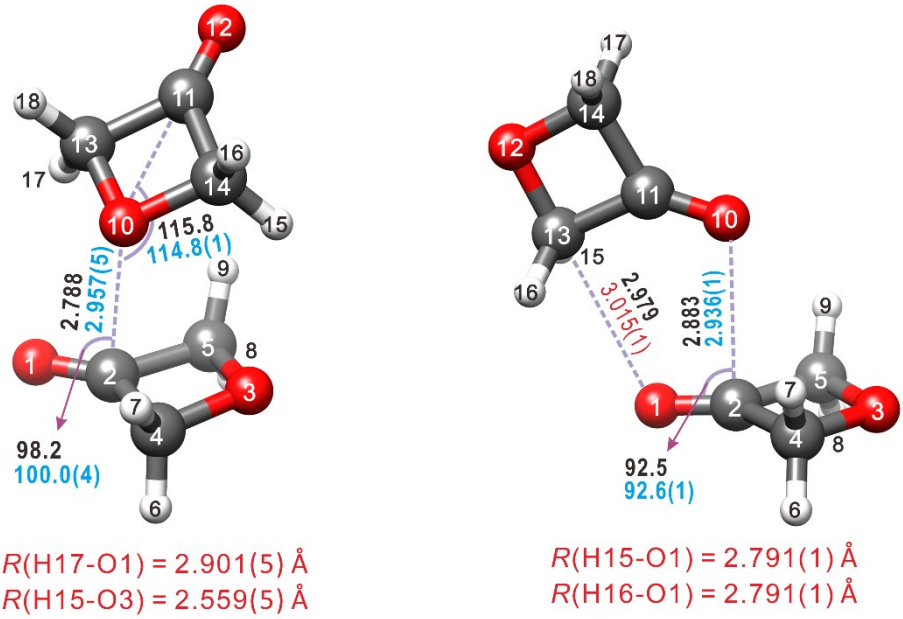

Figure S3 Fitted (blue) and derived (red) r_0 structure parameters of isomers CE1 (left) and CC1 (right). Corresponding r_e parameters (black) are also given for comparison.