Electronic Supplementary Information

for

Conformational analysis of spiro-epoxides by principal component analysis of molecular dynamics trajectories

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Table S1. Total variance represented by principal components calculated for a set of internal coordinate geometries of *cis*-4-methyl-1-oxaspiro[2.5]octane (*cis*-**2**) and *trans*-4-methyl-1-oxaspiro[2.5]octane (*trans*-**2**) from the molecular dynamics run and the number of segments in division of sides for *n*-dimensional parallelepiped

Principal component	*cis*-**2**		*trans*-**2**	
	Variance / %	Number of segments	Variance / %	Number of segments
PC1	27.18	27	27.57	28
PC2	19.20	19	18.91	19
PC3	13.40	13	13.43	13
PC4	13.28	13	13.18	13
PC5	9.38	9	9.59	10
PC6	3.26	3	2.81	3
PC7	2.21	2	2.27	2
PC8	1.84	2	1.92	2
PC9	1.12	2	1.06	2
PC10	1.01	2	0.73	2

Table S2. Total variance represented by principal components calculated for a set of internal coordinate geometries of *cis*-5-methyl-1-oxaspiro[2.5]octane (*cis*-**3**) and *trans*-5-methyl-1-oxaspiro[2.5]octane (*trans*-**3**) from the molecular dynamics run and the number of segments in division of sides for *n*-dimensional parallelepiped

Principal component	*cis*-**3**		*trans*-**3**	
	Variance / %	Number of segments	Variance / %	Number of segments
PC1	27.54	28	37.90	38
PC2	17.87	18	17.03	17
PC3	13.93	14	16.85	17
PC4	13.33	13	11.27	11
PC5	9.85	10	6.15	6
PC6	2.89	3	1.80	2
PC7	2.18	2	1.29	2
PC8	1.85	2	0.86	2
PC9	1.05	2	0.64	2
PC10	0.71	2	0.46	2

Table S3. Total variance represented by principal components calculated for a set of internal coordinate geometries of *cis*-6-methyl-1-oxaspiro[2.5]octane (*cis*-**4**) and *trans*-6-methyl-1-oxaspiro[2.5]octane (*trans*-**4**) from the molecular dynamics run and the number of segments in division of sides for *n*-dimensional parallelepiped

Principal component	*cis*-**4**		*trans*-**4**	
	Variance / %	Number of segments	Variance / %	Number of segments
PC1	27.64	28	26.85	27
PC2	17.90	18	18.22	18
PC3	13.79	14	13.81	14
PC4	13.56	14	13.51	14
PC5	10.23	10	10.21	10
PC6	2.90	3	3.02	3
PC7	2.27	2	2.36	2
PC8	1.81	2	1.87	2
PC9	1.01	2	1.04	2
PC10	0.70	2	0.71	2

Table S4. Relative standard Gibbs energies of formation for compound **2**: 4-methyl-1-oxaspiro[2.5]octane calculated using B3LYP functional and 6-311++G(d,p) basis set with D3 version of Grimme's dispersion. (at *T* = 298.15 K and *p* = 101325 Pa)

Compound	$\Delta_f G°$ / kJ mol^{-1}
cis-4-methyl-1-*O*-*ax*-oxaspiro[2.5]octane	0.39
cis-4-methyl-1-*O*-*eq*-oxaspiro[2.5]octane	2.19
trans-4-methyl-1-*O*-*ax*-oxaspiro[2.5]octane	1.24
trans-4-methyl-1-*O*-*eq*-oxaspiro[2.5]octane	0.00

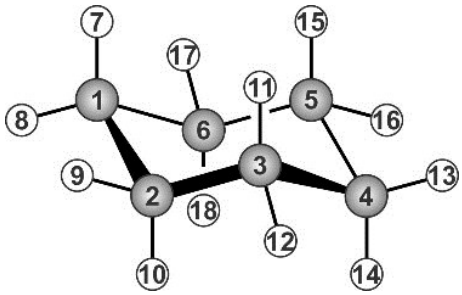
Table S5. Relative standard Gibbs energies of formation for compound **3**: 5-methyl-1-oxaspiro[2.5]octane calculated using B3LYP functional and 6-311++G(d,p) basis set with D3 version of Grimme's dispersion. (at *T* = 298.15 K and *p* = 101325 Pa)

Compound	$\Delta_f G°$ / kJ mol^{-1}
cis-5-methyl-1-*O*-*ax*-oxaspiro[2.5]octane	7.51
cis-5-methyl-1-*O*-*eq*-oxaspiro[2.5]octane	1.23
trans-5-methyl-1-*O*-*ax*-oxaspiro[2.5]octane	0.00
trans-5-methyl-1-*O*-*eq*-oxaspiro[2.5]octane	8.27

Table S6. Relative standard Gibbs energies of formation for compound **4**: 6-methyl-1-oxaspiro[2.5]octane calculated using B3LYP functional and 6-311++G(d,p) basis set with D3 version of Grimme's dispersion. (at *T* = 298.15 K and *p* = 101325 Pa)

Compound	$\Delta_f G°$ / kJ mol^{-1}
cis-6-methyl-1-*O*-*ax*-oxaspiro[2.5]octane	0.00
cis-6-methyl-1-*O*-*eq*-oxaspiro[2.5]octane	8.99
trans-6-methyl-1-*O*-*ax*-oxaspiro[2.5]octane	1.24
trans-6-methyl-1-*O*-*eq*-oxaspiro[2.5]octane	7.79

Table S7. Definition of internal coordinates for cyclohexane used in principal component analysis of the molecular dynamics trajectory.



No	Internal coordinate	1. Atom	2. Atom	3. Atom	4. Atom
1.	*r*	2	1		
2.	*r*	3	2		
3.	*r*	4	3		
4.	*r*	5	4		
5.	*r*	6	1		
6.	*r*	7	1		
7.	*r*	8	1		
8.	*r*	9	2		
9.	*r*	10	2		
10.	*r*	11	3		
11.	*r*	12	3		
12.	*r*	13	4		
13.	*r*	14	4		
14.	*r*	15	5		
15.	*r*	16	5		
16.	*r*	17	6		
17.	*r*	18	6		
18.	*φ*	3	2	1	
19.	*φ*	4	3	2	
20.	*φ*	5	4	3	
21.	*φ*	6	1	2	
22.	*φ*	7	1	2	
23.	*φ*	8	1	2	
24.	*φ*	9	2	1	
25.	*φ*	10	2	1	
26.	*φ*	11	3	2	
27.	*φ*	12	3	2	
28.	*φ*	13	4	3	
29.	*φ*	14	4	3	
30.	*φ*	15	5	4	
31.	*φ*	16	5	4	
32.	*φ*	17	6	1	
33.	*φ*	18	6	1	

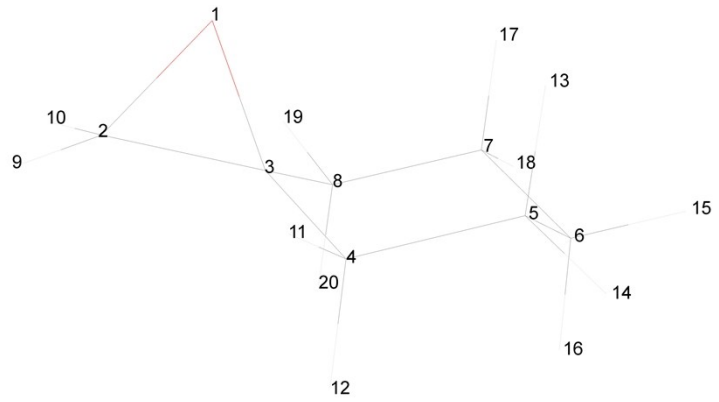
34.	τ	4	3	2	1
35.	τ	5	4	3	2
36.	τ	6	1	2	3
37.	τ	7	1	2	3
38.	τ	8	1	2	3
39.	τ	9	2	1	6
40.	τ	10	2	1	6
41.	τ	11	3	2	1
42.	τ	12	3	2	1
43.	τ	13	4	3	2
44.	τ	14	4	3	2
45.	τ	15	5	4	3
46.	τ	16	5	4	3
47.	τ	17	6	1	2
48.	τ	18	6	1	2

r - distance

φ - bond angle

τ - dihedral angle

Table S8. Definition of internal coordinates for 1-oxaspiro[2,5]octane (**1**) used in principal component analysis of the molecular dynamics trajectory.



No.	Internal coordinate	1. Atom	2. Atom	3. Atom	4. Atom
1.	*r*	2	1		
2.	*r*	3	1		
3.	*r*	4	3		
4.	*r*	5	4		
5.	*r*	6	5		
6.	*r*	7	6		
7.	*r*	8	3		
8.	*r*	9	2		
9.	*r*	10	2		
10.	*r*	11	4		
11.	*r*	12	4		
12.	*r*	13	5		
13.	*r*	14	5		
14.	*r*	15	6		
15.	*r*	16	6		
16.	*r*	17	7		
17.	*r*	18	7		
18.	*r*	19	8		
19.	*r*	20	8		
20.	*φ*	3	1	2	
21.	*φ*	4	3	1	
22.	*φ*	5	4	3	
23.	*φ*	6	5	4	
24.	*φ*	7	6	5	
25.	*φ*	8	3	1	
26.	*φ*	9	2	1	
27.	*φ*	10	2	1	
28.	*φ*	11	4	3	
29.	*φ*	12	4	3	
30.	*φ*	13	5	4	
31.	*φ*	14	5	4	
32.	*φ*	15	6	5	
33.	*φ*	16	6	5	

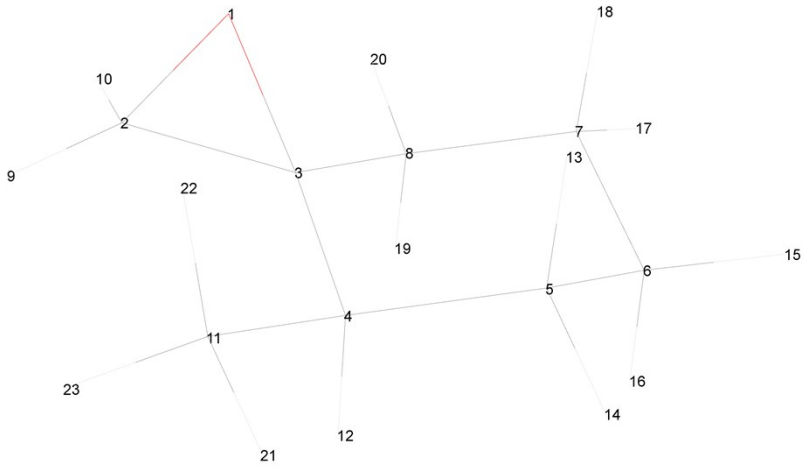
34.	φ	17	7	6	
35.	φ	18	7	6	
36.	φ	19	8	3	
37.	φ	20	8	3	
38.	τ	4	3	1	2
39.	τ	5	4	3	1
40.	τ	6	5	4	3
41.	τ	7	6	5	4
42.	τ	8	3	1	2
43.	τ	9	2	1	3
44.	τ	10	2	1	3
45.	τ	11	4	3	1
46.	τ	12	4	3	1
47.	τ	13	5	4	3
48.	τ	14	5	4	3
49.	τ	15	6	5	4
50.	τ	16	6	5	4
51.	τ	17	7	6	5
52.	τ	18	7	6	5
53.	τ	19	8	3	1
54.	τ	20	8	3	1

r - distance

φ - bond angle

τ - dihedral angle

Table S9. Definition of internal coordinates for *cis*-4-methyl-1-oxaspiro[2.5]octane (*cis*-**2**) used in principal component analysis of the molecular dynamics trajectory.



No.	Internal coordinate	1. Atom	2. Atom	3. Atom	4. Atom
1.	*r*	2	1		
2.	*r*	3	1		
3.	*r*	4	3		
4.	*r*	5	4		
5.	*r*	6	5		
6.	*r*	7	6		
7.	*r*	8	3		
8.	*r*	9	2		
9.	*r*	10	2		
10.	*r*	11	4		
11.	*r*	12	4		
12.	*r*	13	5		
13.	*r*	14	5		
14.	*r*	15	6		
15.	*r*	16	6		
16.	*r*	17	7		
17.	*r*	18	7		
18.	*r*	19	8		
19.	*r*	20	8		
20.	*r*	21	11		
21.	*r*	22	11		
22.	*r*	23	11		
23.	*φ*	3	1	2	
24.	*φ*	4	3	1	
25.	*φ*	5	4	3	
26.	*φ*	6	5	4	
27.	*φ*	7	6	5	
28.	*φ*	8	3	1	
29.	*φ*	9	2	1	
30.	*φ*	10	2	1	

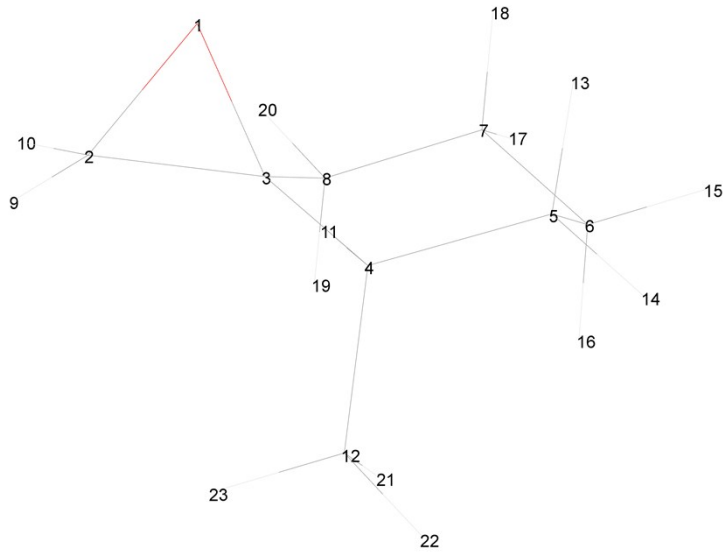
31.	φ	11	4	3	
32.	φ	12	4	3	
33.	φ	13	5	4	
34.	φ	14	5	4	
35.	φ	15	6	5	
36.	φ	16	6	5	
37.	φ	17	7	6	
38.	φ	18	7	6	
39.	φ	19	8	3	
40.	φ	20	8	3	
41.	φ	21	11	4	
42.	φ	22	11	4	
43.	φ	23	11	4	
44.	τ	4	3	1	2
45.	τ	5	4	3	1
46.	τ	6	5	4	3
47.	τ	7	6	5	4
48.	τ	8	3	1	2
49.	τ	9	2	1	3
50.	τ	10	2	1	3
51.	τ	11	4	3	1
52.	τ	12	4	3	1
53.	τ	13	5	4	3
54.	τ	14	5	4	3
55.	τ	15	6	5	4
56.	τ	16	6	5	4
57.	τ	17	7	6	5
58.	τ	18	7	6	5
59.	τ	19	8	3	1
60.	τ	20	8	3	1
61.	τ	21	11	4	3
62.	τ	22	11	4	3
63.	τ	23	11	4	3

r - distance

φ - bond angle

τ - dihedral angle

Table S10. Definition of internal coordinates for *trans*-4-methyl-1-oxaspiro[2.5]octane (*trans*-**2**) used in principal component analysis of the molecular dynamics trajectory.



No.	Internal coordinate	1. Atom	2. Atom	3. Atom	4. Atom
1.	*r*	2	1		
2.	*r*	3	1		
3.	*r*	4	3		
4.	*r*	5	4		
5.	*r*	6	5		
6.	*r*	7	6		
7.	*r*	8	3		
8.	*r*	9	2		
9.	*r*	10	2		
10.	*r*	11	4		
11.	*r*	12	4		
12.	*r*	13	5		
13.	*r*	14	5		
14.	*r*	15	6		
15.	*r*	16	6		
16.	*r*	17	7		
17.	*r*	18	7		
18.	*r*	19	8		
19.	*r*	20	8		
20.	*r*	21	12		
21.	*r*	22	12		
22.	*r*	23	12		
23.	*φ*	3	1	2	
24.	*φ*	4	3	1	
25.	*φ*	5	4	3	
26.	*φ*	6	5	4	
27.	*φ*	7	6	5	
28.	*φ*	8	3	1	

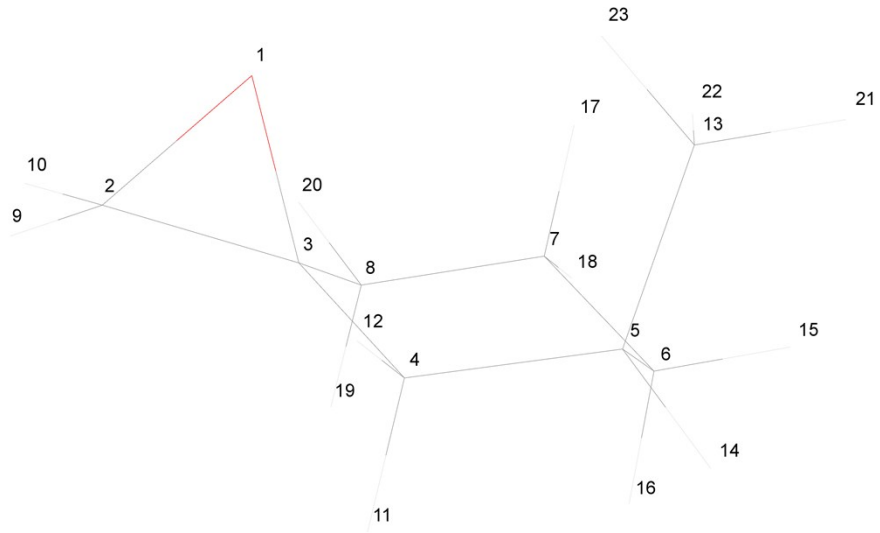
29.	φ	9	2	1	
30.	φ	10	2	1	
31.	φ	11	4	3	
32.	φ	12	4	3	
33.	φ	13	5	4	
34.	φ	14	5	4	
35.	φ	15	6	5	
36.	φ	16	6	5	
37.	φ	17	7	6	
38.	φ	18	7	6	
39.	φ	19	8	3	
40.	φ	20	8	3	
41.	φ	21	12	4	
42.	φ	22	12	4	
43.	φ	23	12	4	
44.	τ	4	3	1	2
45.	τ	5	4	3	1
46.	τ	6	5	4	3
47.	τ	7	6	5	4
48.	τ	8	3	1	2
49.	τ	9	2	1	3
50.	τ	10	2	1	3
51.	τ	11	4	3	1
52.	τ	12	4	3	1
53.	τ	13	5	4	3
54.	τ	14	5	4	3
55.	τ	15	6	5	4
56.	τ	16	6	5	4
57.	τ	17	7	6	5
58.	τ	18	7	6	5
59.	τ	19	8	3	1
60.	τ	20	8	3	1
61.	τ	21	12	4	3
62.	τ	22	12	4	3
63.	τ	23	12	4	3

r - distance

φ - bond angle

τ - dihedral angle

Table S11. Definition of internal coordinates for *cis*-5-methyl-1-oxaspiro[2.5]octane (*cis*-**3**) used in principal component analysis of the molecular dynamics trajectory.



No.	Internal coordinate	1. Atom	2. Atom	3. Atom	4. Atom
1.	*r*	2	1		
2.	*r*	3	1		
3.	*r*	4	3		
4.	*r*	5	4		
5.	*r*	6	5		
6.	*r*	7	6		
7.	*r*	8	3		
8.	*r*	9	2		
9.	*r*	10	2		
10.	*r*	11	4		
11.	*r*	12	4		
12.	*r*	13	5		
13.	*r*	14	5		
14.	*r*	15	6		
15.	*r*	16	6		
16.	*r*	17	7		
17.	*r*	18	7		
18.	*r*	19	8		
19.	*r*	20	8		
20.	*r*	21	13		
21.	*r*	22	13		
22.	*r*	23	13		
23.	*φ*	3	1	2	
24.	*φ*	4	3	1	
25.	*φ*	5	4	3	
26.	*φ*	6	5	4	
27.	*φ*	7	6	5	

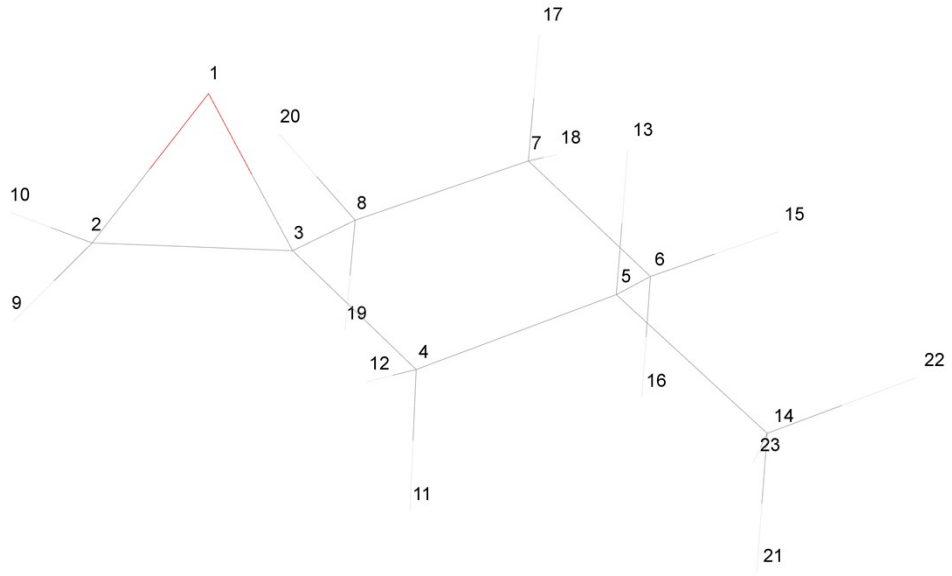
28.	φ	8	3	1	
29.	φ	9	2	1	
30.	φ	10	2	1	
31.	φ	11	4	3	
32.	φ	12	4	3	
33.	φ	13	5	4	
34.	φ	14	5	4	
35.	φ	15	6	5	
36.	φ	16	6	5	
37.	φ	17	7	6	
38.	φ	18	7	6	
39.	φ	19	8	3	
40.	φ	20	8	3	
41.	φ	21	13	5	
42.	φ	22	13	5	
43.	φ	23	13	5	
44.	τ	4	3	1	2
45.	τ	5	4	3	1
46.	τ	6	5	4	3
47.	τ	7	6	5	4
48.	τ	8	3	1	2
49.	τ	9	2	1	3
50.	τ	10	2	1	3
51.	τ	11	4	3	1
52.	τ	12	4	3	1
53.	τ	13	5	4	3
54.	τ	14	5	4	3
55.	τ	15	6	5	4
56.	τ	16	6	5	4
57.	τ	17	7	6	5
58.	τ	18	7	6	5
59.	τ	19	8	3	1
60.	τ	20	8	3	1
61.	τ	21	13	5	4
62.	τ	22	13	5	4
63.	τ	23	13	5	4

r - distance

φ - bond angle

τ - dihedral angle

Table S12. Definition of internal coordinates for *trans*-5-methyl-1-oxaspiro[2.5]octane (*trans*-**3**) used in principal component analysis of the molecular dynamics trajectory.



No.	Internal coordinate	1. Atom	2. Atom	3. Atom	4. Atom
1.	*r*	2	1		
2.	*r*	3	1		
3.	*r*	4	3		
4.	*r*	5	4		
5.	*r*	6	5		
6.	*r*	7	6		
7.	*r*	8	3		
8.	*r*	9	2		
9.	*r*	10	2		
10.	*r*	11	4		
11.	*r*	12	4		
12.	*r*	13	5		
13.	*r*	14	5		
14.	*r*	15	6		
15.	*r*	16	6		
16.	*r*	17	7		
17.	*r*	18	7		
18.	*r*	19	8		
19.	*r*	10	8		
20.	*r*	21	14		
21.	*r*	22	14		
22.	*r*	23	14		
23.	*φ*	3	1	2	
24.	*φ*	4	3	1	
25.	*φ*	5	4	3	
26.	*φ*	6	5	4	
27.	*φ*	7	6	5	

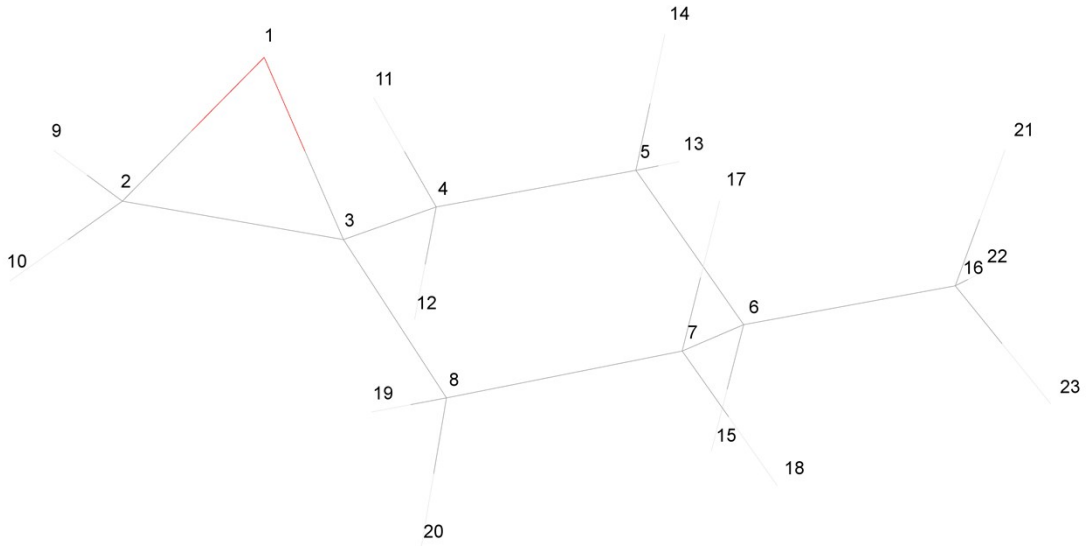
28.	φ	8	3	1	
29.	φ	9	2	1	
30.	φ	10	2	1	
31.	φ	11	4	3	
32.	φ	12	4	3	
33.	φ	13	5	4	
34.	φ	14	5	4	
35.	φ	15	6	5	
36.	φ	16	6	5	
37.	φ	17	7	6	
38.	φ	18	7	6	
39.	φ	19	8	3	
40.	φ	10	8	3	
41.	φ	21	14	5	
42.	φ	22	14	5	
43.	φ	23	14	5	
44.	τ	4	3	1	2
45.	τ	5	4	3	1
46.	τ	6	5	4	3
47.	τ	7	6	5	4
48.	τ	8	3	1	2
49.	τ	9	2	1	3
50.	τ	10	2	1	3
51.	τ	11	4	3	1
52.	τ	12	4	3	1
53.	τ	13	5	4	3
54.	τ	14	5	4	3
55.	τ	15	6	5	4
56.	τ	16	6	5	4
57.	τ	17	7	6	5
58.	τ	18	7	6	5
59.	τ	19	8	3	1
60.	τ	10	8	3	1
61.	τ	21	14	5	4
62.	τ	22	14	5	4
63.	τ	23	14	5	4

r - distance

φ - bond angle

τ - dihedral angle

Table S13. Definition of internal coordinates for *cis*-6-methyl-1-oxaspiro[2.5]octane (*cis*-**4**) used in principal component analysis of the molecular dynamics trajectory.



No.	Internal coordinate	1. Atom	2. Atom	3. Atom	4. Atom
1.	*r*	2	1		
2.	*r*	3	1		
3.	*r*	4	3		
4.	*r*	5	4		
5.	*r*	6	5		
6.	*r*	7	6		
7.	*r*	8	3		
8.	*r*	9	2		
9.	*r*	10	2		
10.	*r*	11	4		
11.	*r*	12	4		
12.	*r*	13	5		
13.	*r*	14	5		
14.	*r*	15	6		
15.	*r*	16	6		
16.	*r*	17	7		
17.	*r*	18	7		
18.	*r*	19	8		
19.	*r*	20	8		
20.	*r*	21	16		
21.	*r*	22	16		
22.	*r*	23	16		
23.	*φ*	3	1	2	
24.	*φ*	4	3	1	
25.	*φ*	5	4	3	
26.	*φ*	6	5	4	
27.	*φ*	7	6	5	

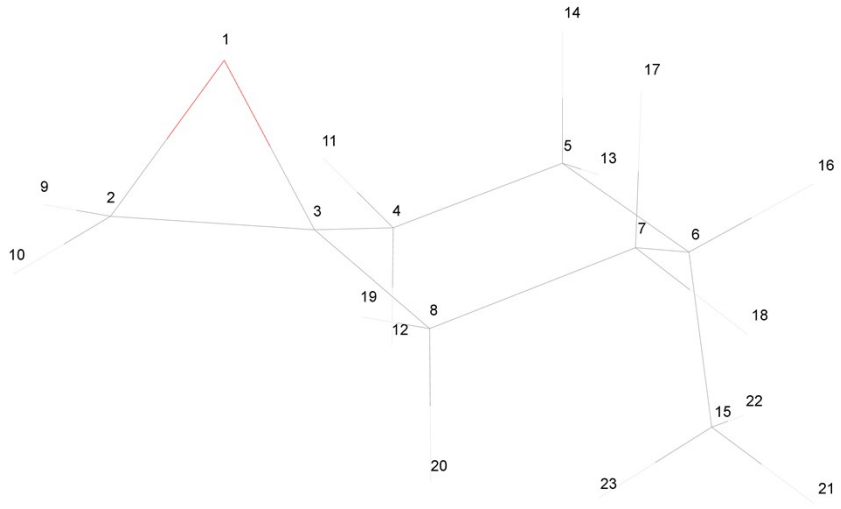
28.	φ	8	3	1	
29.	φ	9	2	1	
30.	φ	10	2	1	
31.	φ	11	4	3	
32.	φ	12	4	3	
33.	φ	13	5	4	
34.	φ	14	5	4	
35.	φ	15	6	5	
36.	φ	16	6	5	
37.	φ	17	7	6	
38.	φ	18	7	6	
39.	φ	19	8	3	
40.	φ	20	8	3	
41.	φ	21	16	6	
42.	φ	22	16	6	
43.	φ	23	16	6	
44.	τ	4	3	1	2
45.	τ	5	4	3	1
46.	τ	6	5	4	3
47.	τ	7	6	5	4
48.	τ	8	3	1	2
49.	τ	9	2	1	3
50.	τ	10	2	1	3
51.	τ	11	4	3	1
52.	τ	12	4	3	1
53.	τ	13	5	4	3
54.	τ	14	5	4	3
55.	τ	15	6	5	4
56.	τ	16	6	5	4
57.	τ	17	7	6	5
58.	τ	18	7	6	5
59.	τ	19	8	3	1
60.	τ	20	8	3	1
61.	τ	21	16	6	5
62.	τ	22	16	6	5
63.	τ	23	16	6	5

r - distance

φ - bond angle

τ - dihedral angle

Table S14. Definition of internal coordinates for *trans*-6-methyl-1-oxaspiro[2.5]octane (*trans*-**4**) used in principal component analysis of the molecular dynamics trajectory.



No.	Internal coordinate	1. Atom	2. Atom	3. Atom	4. Atom
1.	*r*	2	1		
2.	*r*	3	1		
3.	*r*	4	3		
4.	*r*	5	4		
5.	*r*	6	5		
6.	*r*	7	6		
7.	*r*	8	3		
8.	*r*	9	2		
9.	*r*	10	2		
10.	*r*	11	4		
11.	*r*	12	4		
12.	*r*	13	5		
13.	*r*	14	5		
14.	*r*	15	6		
15.	*r*	16	6		
16.	*r*	17	7		
17.	*r*	18	7		
18.	*r*	19	8		
19.	*r*	20	8		
20.	*r*	21	15		
21.	*r*	22	15		
22.	*r*	23	15		
23.	*φ*	3	1	2	
24.	*φ*	4	3	1	
25.	*φ*	5	4	3	
26.	*φ*	6	5	4	
27.	*φ*	7	6	5	
28.	*φ*	8	3	1	
29.	*φ*	9	2	1	
30.	*φ*	10	2	1	

31.	φ	11	4	3	
32.	φ	12	4	3	
33.	φ	13	5	4	
34.	φ	14	5	4	
35.	φ	15	6	5	
36.	φ	16	6	5	
37.	φ	17	7	6	
38.	φ	18	7	6	
39.	φ	19	8	3	
40.	φ	20	8	3	
41.	φ	21	15	6	
42.	φ	22	15	6	
43.	φ	23	15	6	
44.	τ	4	3	1	2
45.	τ	5	4	3	1
46.	τ	6	5	4	3
47.	τ	7	6	5	4
48.	τ	8	3	1	2
49.	τ	9	2	1	3
50.	τ	10	2	1	3
51.	τ	11	4	3	1
52.	τ	12	4	3	1
53.	τ	13	5	4	3
54.	τ	14	5	4	3
55.	τ	15	6	5	4
56.	τ	16	6	5	4
57.	τ	17	7	6	5
58.	τ	18	7	6	5
59.	τ	19	8	3	1
60.	τ	20	8	3	1
61.	τ	21	15	6	5
62.	τ	22	15	6	5
63.	τ	23	15	6	5

r - distance

φ - bond angle

τ - dihedral angle

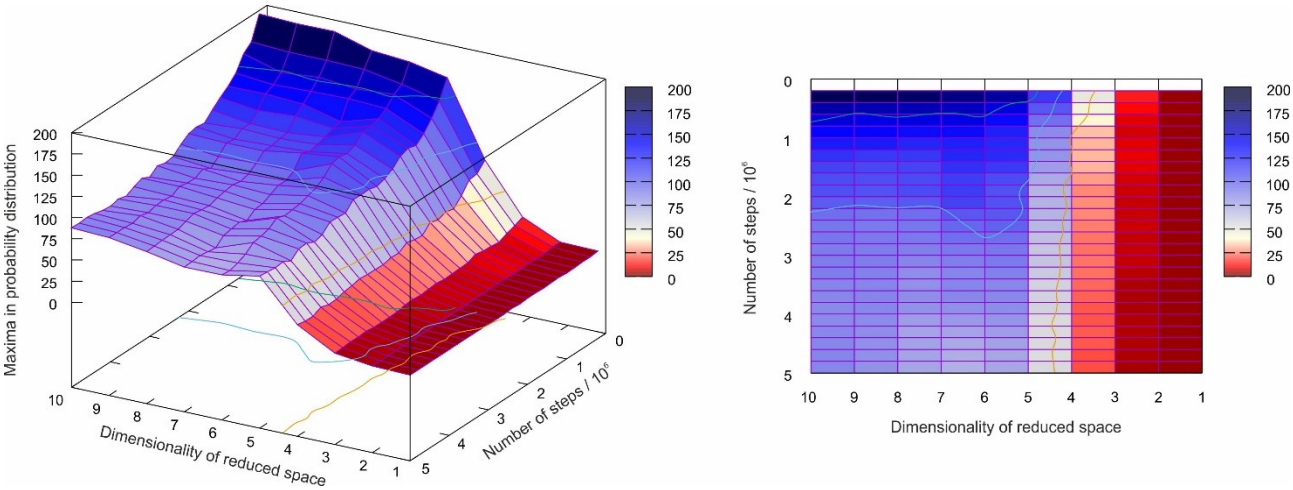


Figure S1. Total number of determined strict local maxima in the probability distribution of *cis*-4-methyl-1-oxaspiro[2.5]octane (*cis*-**2**) geometries in reduced space calculated by principal component analysis of the molecular dynamics trajectory.

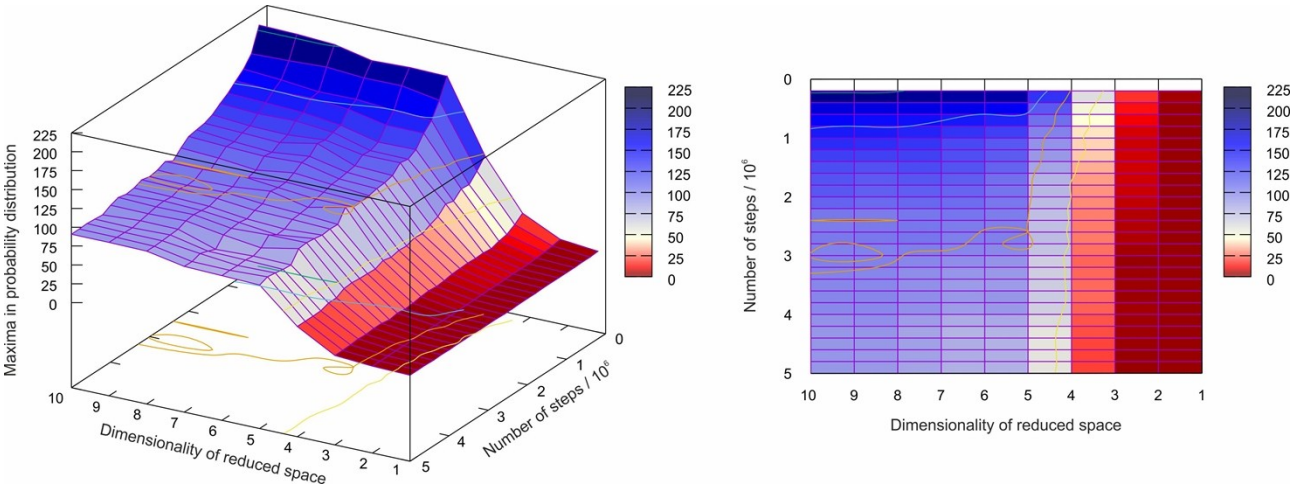


Figure S2. Total number of determined strict local maxima in the probability distribution of *trans*-4-methyl-1-oxaspiro[2.5]octane (*trans*-**2**) geometries in reduced space calculated by principal component analysis of the molecular dynamics trajectory.

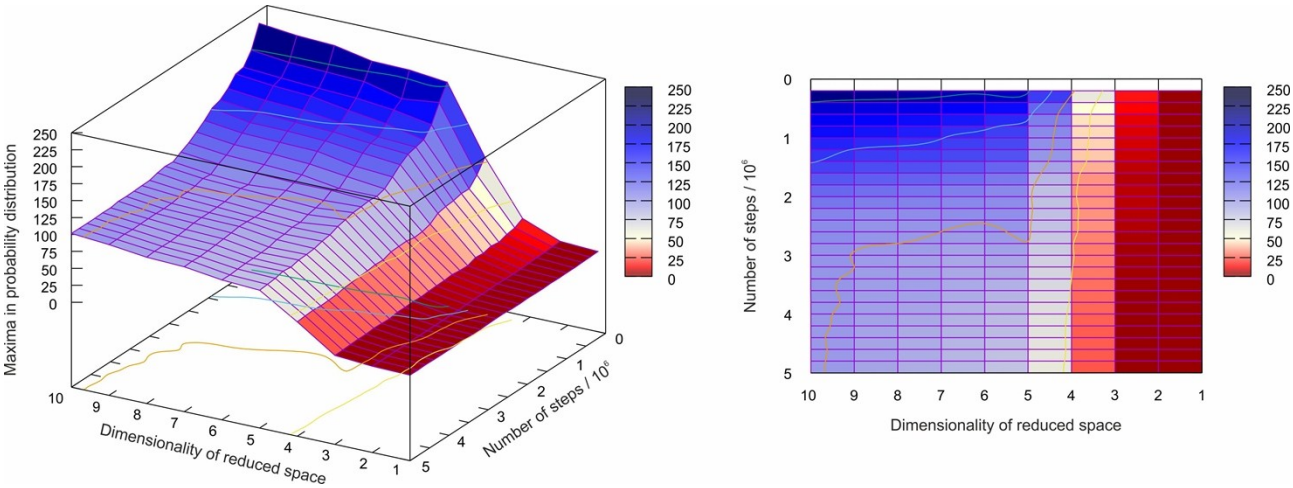


Figure S3. Total number of determined strict local maxima in the probability distribution of *cis*-5-methyl-1-oxaspiro[2.5]octane (*cis*-**3**) geometries in reduced space calculated by principal component analysis of the molecular dynamics trajectory.

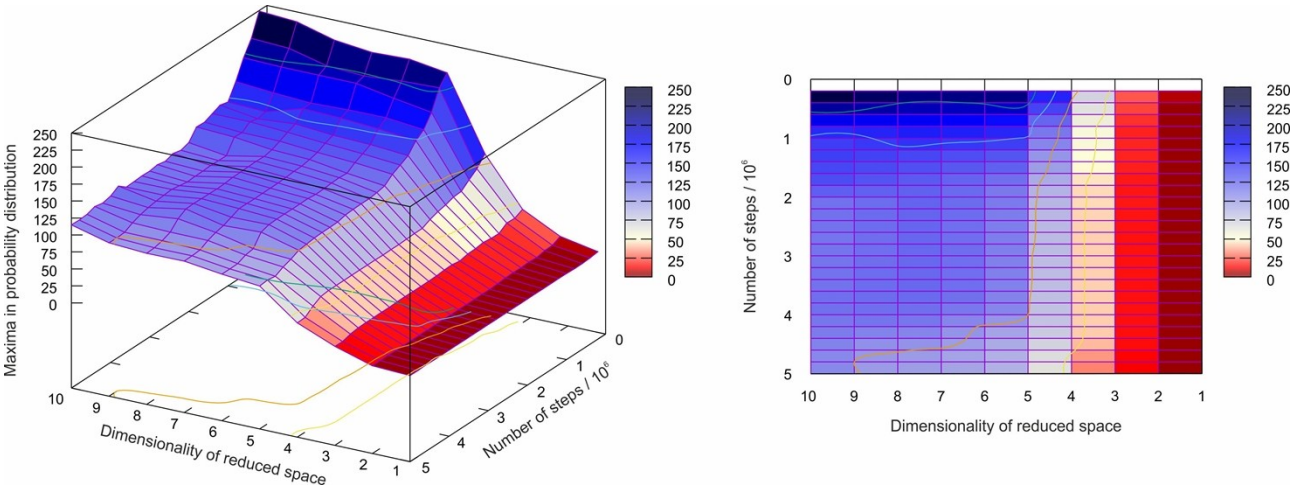


Figure S4. Total number of determined strict local maxima in the probability distribution of *trans*-5-methyl-1-oxaspiro[2.5]octane (*trans*-**3**) geometries in reduced space calculated by principal component analysis of the molecular dynamics trajectory.

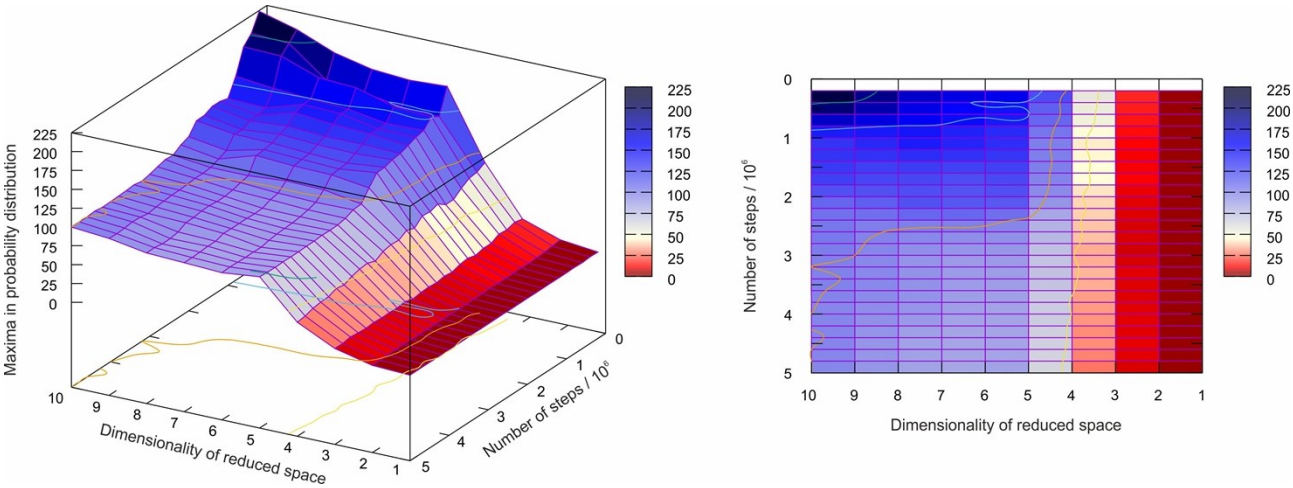


Figure S5. Total number of determined strict local maxima in the probability distribution of *cis*-6-methyl-1-oxaspiro[2.5]octane (*cis*-**4**) geometries in reduced space calculated by principal component analysis of the molecular dynamics trajectory.

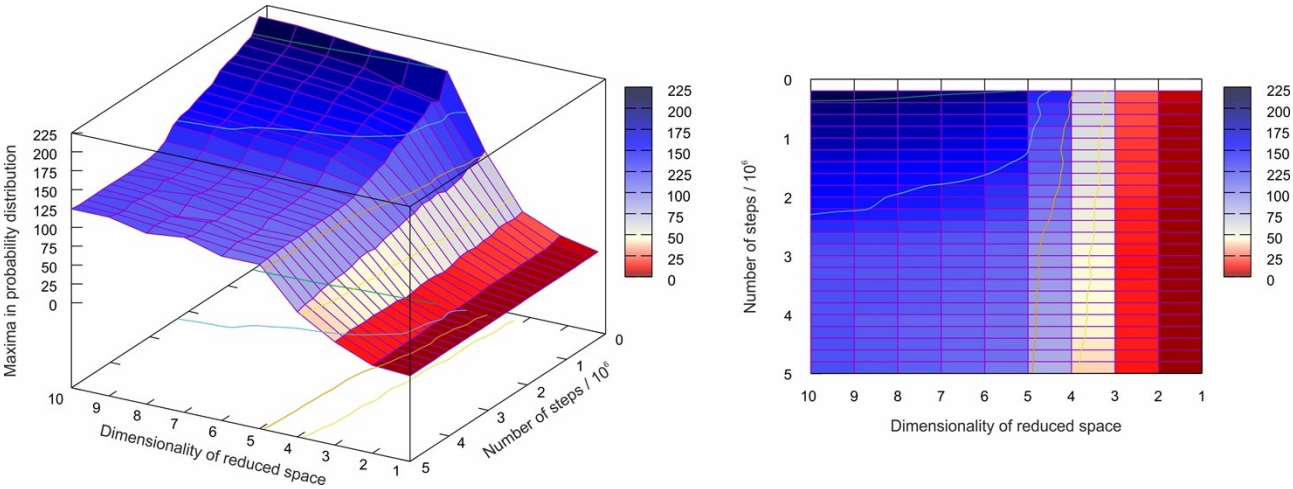


Figure S6. Total number of determined strict local maxima in the probability distribution of *trans*-6-methyl-1-oxaspiro[2.5]octane (*trans*-**4**) geometries in reduced space calculated by principal component analysis of the molecular dynamics trajectory.

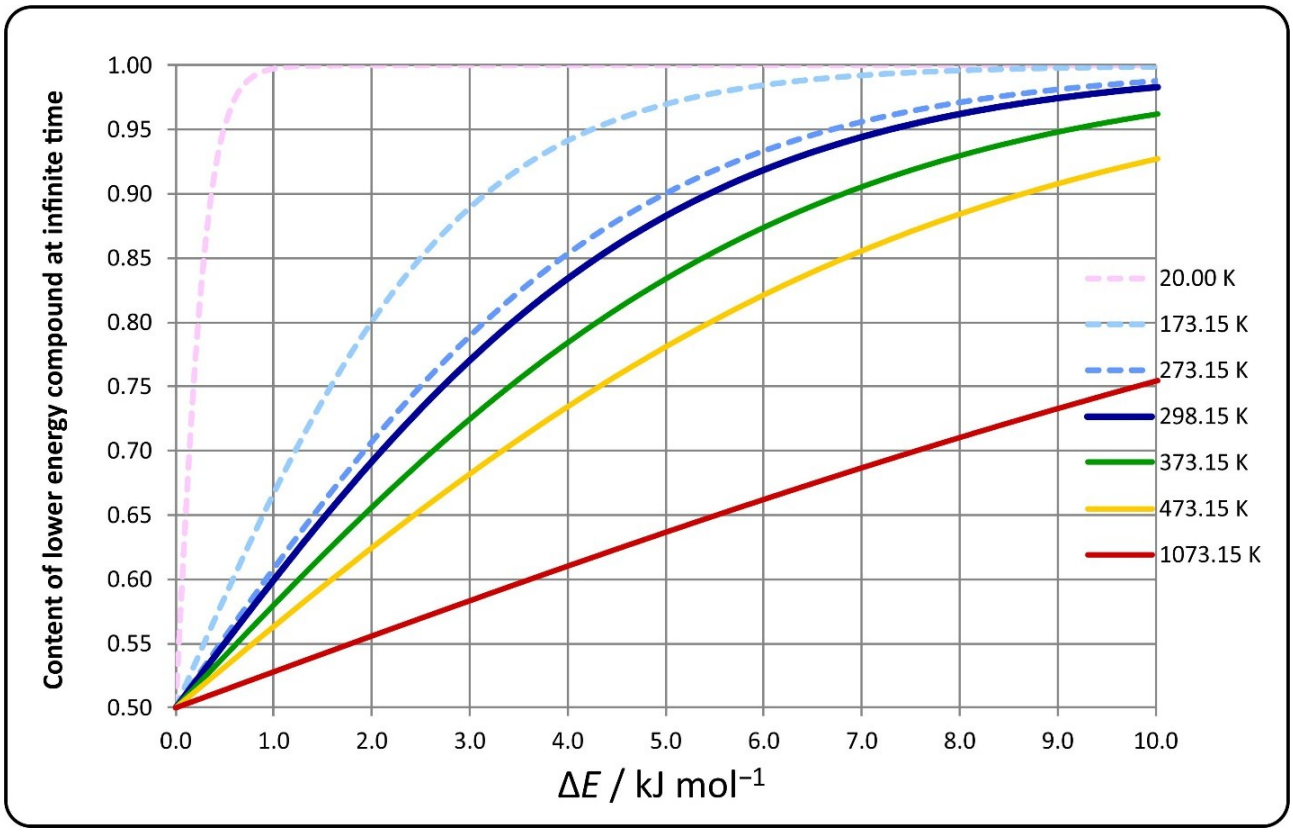
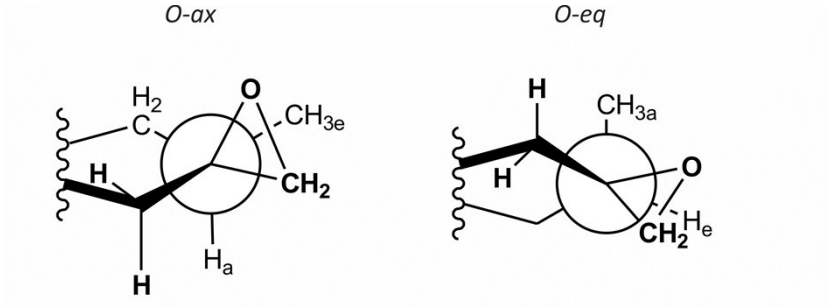


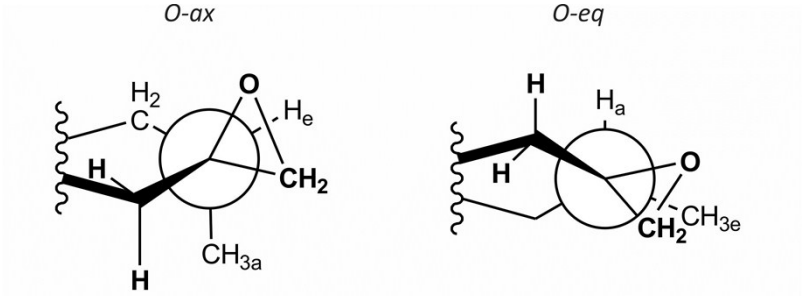
Figure S7. Content of lower energy compound at infinite time in binary system according to the Boltzmann distribution.



torsional angle (H_aCCO)= 165.6°
torsional angle (CH_{3e}CCO)= -45.9°
torsional angle (CH_{3e}CC**CH_2**)= -22.3°
torsional angle (H_aCC**CH_2**)= -97.4°

torsional angle (CH_{3a}CCO)= -66.6°
torsional angle (H_eCCO)= -50.6°
torsional angle (H_eCC**CH_2**)= 17.0°
torsional angle (CH_{3a}CC**CH_2**)= -134.2°

Figure S8. Newman projections through the cyclohexane spiro-carbon-carbon bond in *O-ax* and *O-eq* chair-like conformers of *cis*-**2**.



torsional angle (CH_{3a}CCO)= -152.3°
torsional angle (H_eCCO)= -34.4°
torsional angle (H_eCC**CH_2**)= 32.6°
torsional angle (CH_{3a}CC**CH_2**)= -85.3°

torsional angle (H_aCCO)= 76.4°
torsional angle (CH_{3e}CCO)= -42.0°
torsional angle (CH_{3e}CC**CH_2**)= 26.9°
torsional angle (H_aCC**CH_2**)= 145.3°

Figure S9. Newman projections through the cyclohexane spiro-carbon-carbon bond in *O-ax* and *O-eq* chair-like conformers of *trans*-**2**.

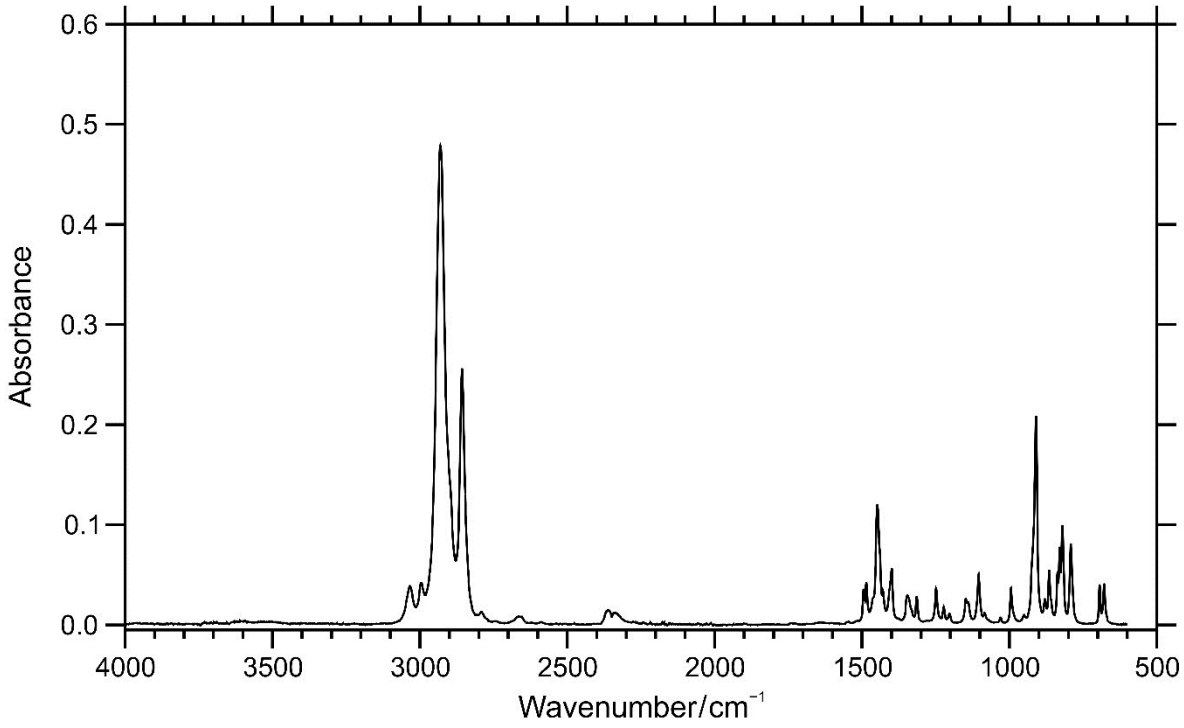


Figure S10. Experimental IR spectra of 1-oxaspiro[2.5]octane.