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Supporting Information

Electronic Transitions in Conformationally Controlled Tetrasilanes with a Wide Range of SiSiSiSi Dihedral Angles

Hayato Tsuji,[a, f] Heather A. Fogarty,[b] Masahiro Ehara,[c, d, g] Ryoichi Fukuda,[c, d, g] Deborah L. Casher,[b] Kohei Tamao,[a, i] Hiroshi Nakatsuji,[c, d, h] and Josef Michl*[b, e]

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Supporting Information

Contents

1. Geometry and Computational Dimensions

Table S1. SiSiSiSi dihedral angle (ω) and SiSiSi valence angle (δ) in tetrasilanes calculated with B3LYP/6-311G*.

Molecule	Theory (present)			Theory (previous)[a]
	Structure	ω (°)	δ (°)	ω (°)
1	C_s	0	100.3	
2a	C_2	36.7	105.7	38
2b	C_2	44.9	105.1	50
3a	C_2	53.9	107.6	55
3c	C_1	42.2	113.2	43
3d	C_2	28.6	111.6	30
4a	C_1	43.4	112.9	65
4b	C_2	61.4	117.8	63
4d	C_2	78.1	115.9	80
5	C_2	23.5	118.8	
6	C_1	119.6	118.2, 118.8	95.4
7	C_{2h}	180	116.7	
10t	C_2	165.2	113.1	164
10o	C_2	95.6	114.3	92
10g	C_2	54.2	115.5	54

[a] Ref. [50] for **1 - 4** and **10**, Ref. [53] for **6**.

Table S2. Computational dimensions of SAC-CI.

Molecule	AO	Active space orbitals		SAC	SAC-CI
		occupied	unoccupied	(after selection)	(after selection)
1	246	39	178	221,356	405,402 (A')
					409,705 (A")
2	260	42	188	222,364	478,563 (A)
					474,781 (B)
3	274	45	198	227,581	486,412 (A)
					505,162 (B)
4	288	48	208	216,239	522,141 (A)
					524,865 (B)
5	340	59	245	214,330	449,225(A)
					442,614(B)
6	416	75	299	72,221	774,449 (A)
7	340	59	245	304,351	298,418 (A_u)
					255,126 (B_u)
10 (ortho)	264	43	191	210,130	478,331 (A)
					465,309 (B)

2. SAC-CI Results for 1 - 7 and *n*-Si_4Me_{10} (10) (gauche, ortho, transoid)

Table S3. SAC-CI results for excitation energies (ΔE) and oscillator strengths (f) of **1 - 4**, $Si_4Me_8(CH_2)_n$ (n = 1 - 4).

Molecule	ω/δ [a]	ΔE		f
		eV	10^3 cm^{-1}	
1: $Si_4Me_8CH_2$	0.0 º /			
A′	100.3 º	4.707	38.0	0.001
		5.740	46.3	0.085
		6.480	52.3	0.089
		7.014	56.6	0.027
		7.244	58.4	0.004
A″		5.484	44.2	0.001
		6.273	50.6	0.229
		6.442	52.0	0.097
		7.172	57.8	0.038
		6.647	53.6	0.068
2b: $Si_4Me_8(CH_2)_2$	44.9 º /			
A	105.1 º	5.744	46.3	0.017
		5.788	46.7	0.053
		6.873	55.4	0.025
		7.136	57.6	0.045
		7.542	60.8	0.086
B		5.300	42.7	0.030
		6.057	48.9	0.192
		6.847	55.2	0.257
		7.005	56.5	0.147
		7.266	58.6	0.003
3a: $Si_4Me_8(CH_2)_3$	53.9 º /			
A	107.6 º	5.712	46.1	0.018
		5.988	48.3	0.039
		6.636	53.5	0.020
		7.028	56.7	0.085
		7.294	58.8	0.028
B		5.214	42.1	0.051
		6.363	51.3	0.319
		6.662	53.7	0.086
		6.534	52.7	0.066
		7.779	62.7	0.146
4b: $Si_4Me_8(CH_2)_4$	61.4 º /			
A	117.8 º	5.895	47.5	0.012
		6.168	49.7	0.036
		6.896	55.6	0.004
		7.167	57.8	0.060
		7.617	61.4	0.031
B		5.517	44.5	0.089
		6.428	51.8	0.249
		6.879	55.5	0.270
		6.937	55.9	0.222
		7.899	63.7	0.384

[a] ω is the SiSiSiSi dihedral angle and δ is the SiSiSi valence angle.

Table S4. SAC-CI results for excitation energies (ΔE) and oscillator strengths (f) of **5** - **7**.

Molecule	ω/δ [a]	ΔE		f
		eV	(10^3) cm^{-1}	
5	23.5º /			
A	118.8º	5.813	46.9	0.039
		5.789	46.7	0.041
		6.748	54.4	0.000
B		5.502	44.4	0.016
		5.882	47.4	0.227
		6.586	53.1	0.152
6	119.6º /			
A	118.2, 118.8º	5.374	43.3	0.243
		5.494	44.3	0.080
		5.820	46.9	0.023
		5.968	48.1	0.054
		6.157	49.7	0.148
		6.229	50.2	0.076
7	180.0º /			
A_g	116.7º	6.039	48.7	0.000
		6.578	53.0	0.000
B_g		6.658	53.7	0.000
		7.026	56.7	0.000
A_u		5.966	48.1	0.002
		6.674	53.8	0.072
B_u		5.337	43.0	0.408
		5.709	46.0	0.010

[a] ω is the SiSiSiSi dihedral angle and δ is the SiSiSi valence angle.

Table S5. Excitation energies (ΔE) and oscillator strengths (f) of conformers of n-Si_4Me_{10} calculated by the direct SAC-CI method at the three local minima.

Conformer	ΔE		f
State	(eV)	(cm^{-1})	
Gauche			
2A	5.746	46.3	0.021
3A	6.326	51.0	0.034
4A	7.016	56.6	0.041
5A	6.982	56.3	0.000
6A	7.654	61.7	0.004
1B	5.617	45.3	0.057
2B	6.281	50.7	0.248
3B	6.931	55.9	0.353
4B	7.075	57.1	0.213
5B	8.062	65.0	0.333
Ortho			
2A	5.521	44.5	0.004
3A	6.421	51.8	0.038
4A	6.774	54.6	0.055
5A	7.201	58.1	0.008
6A	7.571	61.1	0.026
1B	5.562	44.9	0.194
2B	6.410	51.7	0.239
3B	6.779	54.7	0.113
4B	6.930	55.9	0.149
5B	8.089	65.2	0.496
Transoid			
2A	5.574	45.0	0.005
3A	6.722	54.2	0.001
4A	6.888	55.6	0.152
5A	7.349	59.3	0.001
6A	7.798	62.9	0.020
1B	5.529	44.6	0.458
2B	6.547	52.8	0.027
3B	6.526	52.6	0.019
4B	7.069	57.0	0.001
5B	7.728	62.3	0.083

3. SAC-CI Results for *n*-Si_4Me_{10} (10) at Dihedral Angles ω = 0º to 180º

Table S6. Excitation energies (ΔE) and oscillator strengths (f) of *n*-Si_4Me_{10} at dihedral angles ω = 0 - 75º calculated by the direct SAC-CI method.

State	ΔE		f	State	ΔE		f
	(eV)	(cm^{-1})			(eV)	(cm^{-1})	
ω=0º				ω=15º			
$1A_1$	6.078	49022	0.052	2A	5.981	48243	0.040
$1A_2$	6.092	49132	0.000	3A	6.036	48680	0.014
$2A_1$	7.224	58265	0.010	4A	7.152	57686	0.024
$2A_2$	7.413	59935	0.000	5A	7.250	58478	0.004
$3A_1$	7.444	60043	0.019	6A	7.631	61548	0.113
$1B_1$	5.624	45362	0.000	1B	5.541	44692	0.009
$1B_2$	6.279	50644	0.217	2B	6.230	50251	0.216
$2B_2$	7.039	56774	0.663	3B	7.016	56586	0.609
$2B_1$	7.068	57009	0.196	4B	7.065	56986	0.198
$3B_2$	7.514	60604	0.179	5B	7.846	63279	0.237
ω=30º				ω=45º			
2A	5.955	48030	0.031	2A	5.847	47158	0.025
3A	6.162	49697	0.022	3A	6.285	50693	0.033
4A	7.136	57556	0.037	4A	7.045	56818	0.004
5A	7.141	57597	0.000	5A	7.098	57247	0.037
6A	7.493	60431	0.002	6A	7.640	61617	0.000
1B	5.602	45183	0.028	1B	5.627	45386	0.048
2B	6.282	50671	0.220	2B	6.291	50740	0.242
3B	7.008	56527	0.525	3B	6.970	56217	0.397
4B	7.084	57135	0.216	4B	7.100	57261	0.215
5B	7.829	63146	0.073	5B	8.057	64986	0.477
ω=60º				ω=75º			
2A	5.693	45913	0.018	2A	5.691	45903	0.010
3A	6.346	51185	0.035	3A	6.363	51321	0.037
4A	6.946	56022	0.011	4A	6.859	55322	0.043
5A	6.980	56293	0.032	5A	7.114	57376	0.016
6A	7.653	61725	0.007	6A	7.635	61578	0.021
1B	5.624	45363	0.063	1B	5.647	45548	0.136
2B	6.273	50598	0.248	2B	6.338	51120	0.238
3B	6.929	55882	0.343	3B	6.899	55645	0.159
4B	7.077	57079	0.209	4B	7.047	56836	0.307
5B	7.661	61793	0.058	5B	7.774	62700	0.042

Table S6. (cont) Excitation energies (ΔE) and oscillator strengths (f) of n-Si_4Me_{10} at dihedral angles ω = 90 - 165º calculated by the direct SAC-CI method.

State	ΔE		f	State	ΔE		f
	(eV)	(cm^{-1})			(eV)	(cm^{-1})	
ω=90º				ω=105º			
2A	5.577	44984	0.006	2A	5.455	44001	0.002
3A	6.398	51600	0.038	3A	6.437	51917	0.034
4A	6.807	54901	0.052	4A	6.732	54295	0.062
5A	7.168	57816	0.011	5A	7.233	58335	0.004
6A	7.601	61305	0.023	6A	7.565	61015	0.028
1B	5.589	45078	0.171	1B	5.541	44690	0.220
2B	6.391	51550	0.244	2B	6.421	51790	0.228
3B	6.822	55022	0.130	3B	6.737	54340	0.100
4B	6.966	56183	0.192	4B	6.895	55609	0.120
5B	7.868	63457	0.047	5B	8.059	64997	0.451
ω=120º				ω=135º			
2A	5.420	43718	0.000	2A	5.424	43744	0.001
3A	6.496	52394	0.024	3A	6.575	53028	0.011
4A	6.667	53775	0.083	4A	6.696	54006	0.109
5A	7.333	59141	0.000	5A	7.350	59284	0.000
6A	7.661	61793	0.025	6A	7.719	62258	0.015
1B	5.514	44473	0.298	1B	5.493	44302	0.359
2B	6.479	52258	0.169	2B	6.512	52523	0.080
3B	6.615	53350	0.090	3B	6.563	52932	0.116
4B	6.862	55344	0.061	4B	6.879	55482	0.014
5B	7.948	64107	0.236	5B	7.983	64388	0.199
ω=150º				ω=165º			
2A	5.498	44340	0.004	2A	5.573	44945	0.005
3A	6.656	53687	0.002	3A	6.723	54221	0.001
4A	6.790	54765	0.136	4A	6.888	55553	0.151
5A	7.352	59294	0.000	5A	7.350	59280	0.001
6A	7.798	62897	0.006	6A	7.798	62892	0.020
1B	5.508	44427	0.417	1B	5.529	44592	0.457
2B	6.515	52544	0.030	2B	6.527	52645	0.019
3B	6.545	52785	0.080	3B	6.547	52803	0.028
4B	6.975	56258	0.003	4B	7.068	57008	0.001
5B	7.918	63861	0.176	5B	7.728	62331	0.082

Table S6. (cont) Excitation energies (ΔE) and oscillator strengths (f) of n-Si_4Me_{10} at ω = 180º calculated by the direct SAC-CI method.

State	ΔE		f
	(eV)	(cm^{-1})	
ω=180º			
2A	5.746	46341	0.006
3A	6.827	55065	0.000
4A	7.016	56584	0.159
5A	7.314	58992	0.000
6A	7.476	60297	0.000
1B	5.633	45436	0.470
2B	6.621	53400	0.020
3B	6.673	53821	0.000
4B	7.189	57980	0.000
5B	7.698	62088	0.030

Table S7. Excitation character of 1B and 2B states of n-Si_4Me_{10} at ω = 0 - 180º calculated by the direct SAC-CI method.

State	Character
ω=0º, 15º, 30º, 45º	
1B	H → L ($\sigma_2\pi^*$)
2B	H-1 → L+1 ($\sigma_1\sigma^*$)
ω=60º, 75º, 90º, 105º	
1B	H → L+1 ($\sigma_2\pi^*$)
2B	H-1 → L ($\sigma_1\sigma^*$)
ω=120º, 135º, 150º, 165º, 180º	
1B	H → L ($\sigma_2\sigma^*$)
2B	H-1 → L+1 ($\sigma_1\pi^*$)

4. Polarized Absorption Spectra of 5 - 7

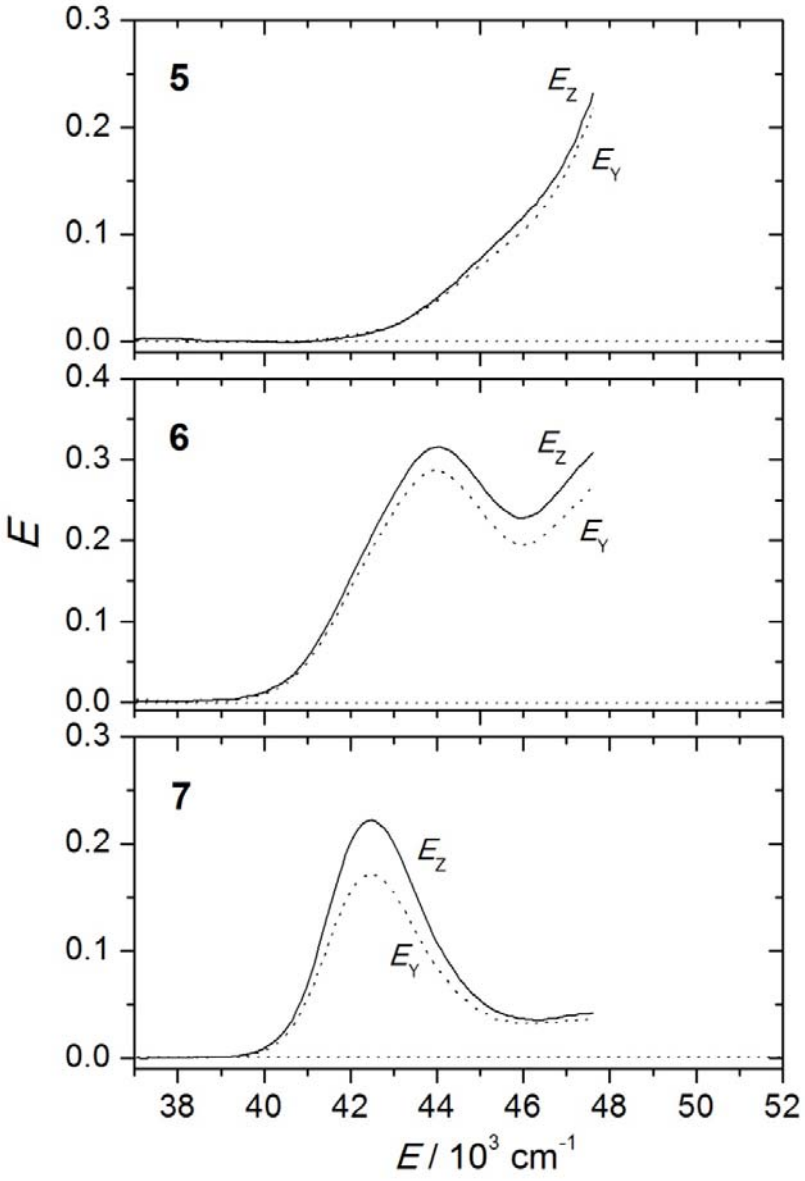


Figure S1. Polarized absorption spectra of **5 - 7**.

5. Structures of *n*-Si_4Me_{10} (10), 1 - 4 ($Si_4Me_8(CH_2)_n$, *n* = 1 - 4), and 5 - 7.

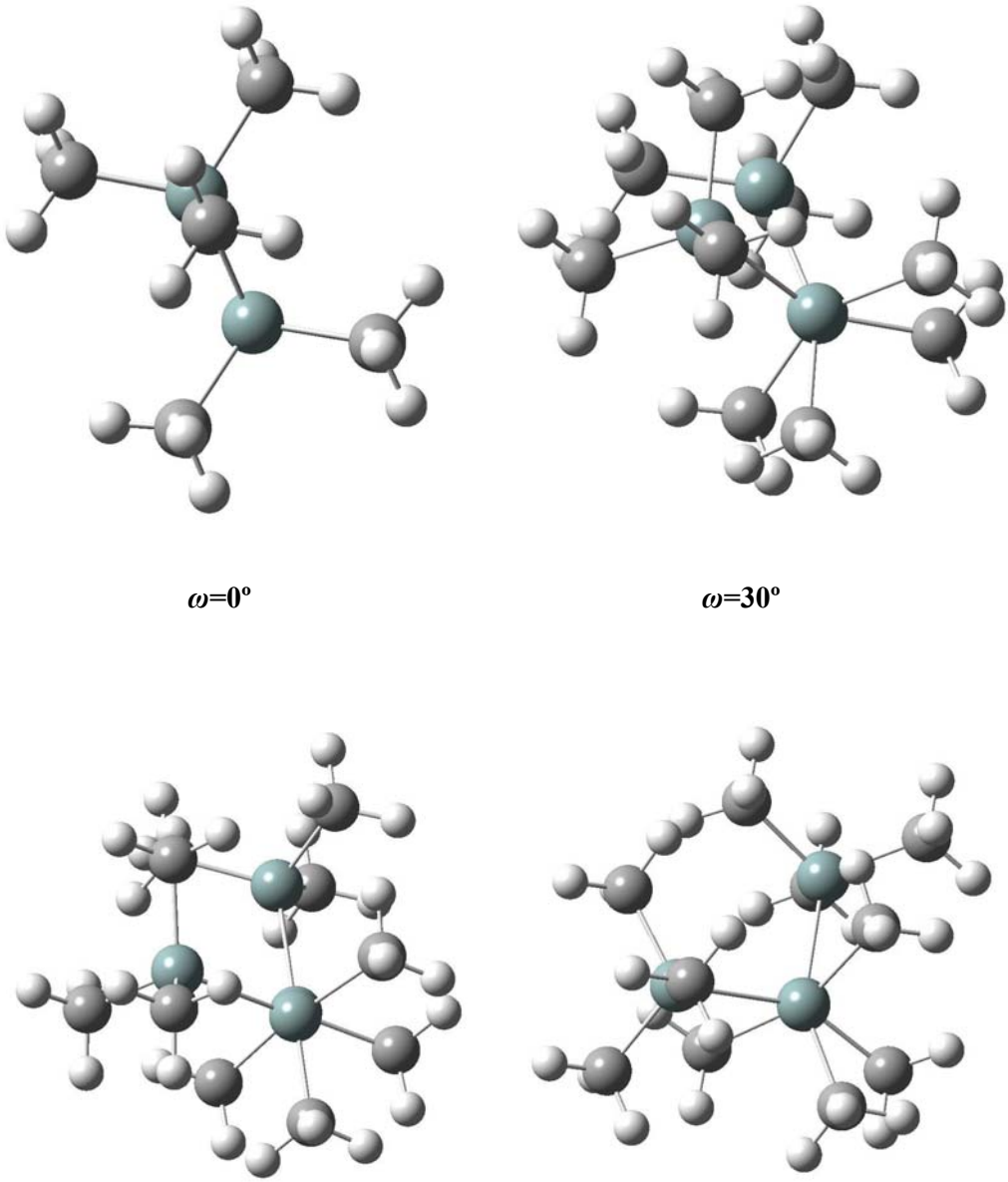
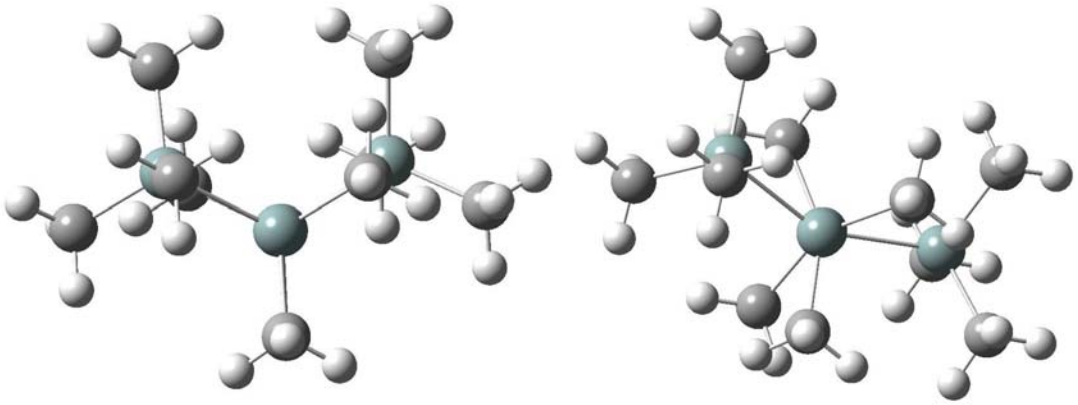
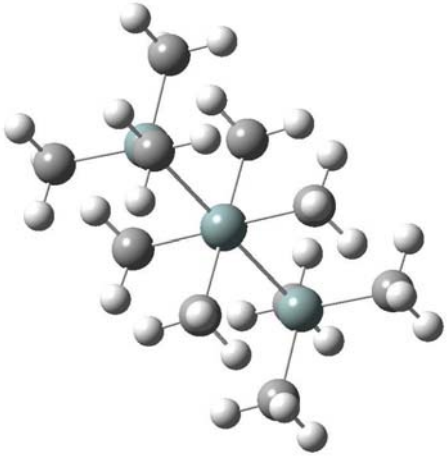


Figure S2. Structures of *n*-Si_4Me_{10} (**10**) at dihedral angles ω = 0 - 180º

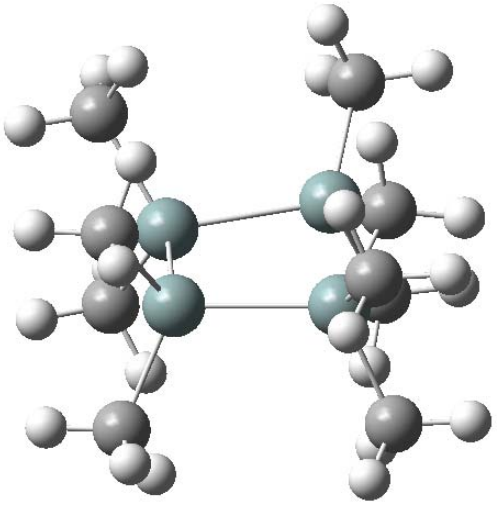


***ω*=120º** ***ω*=150º**

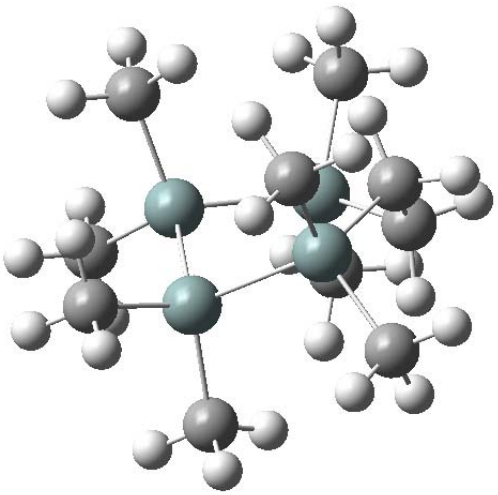


***ω*=180º**

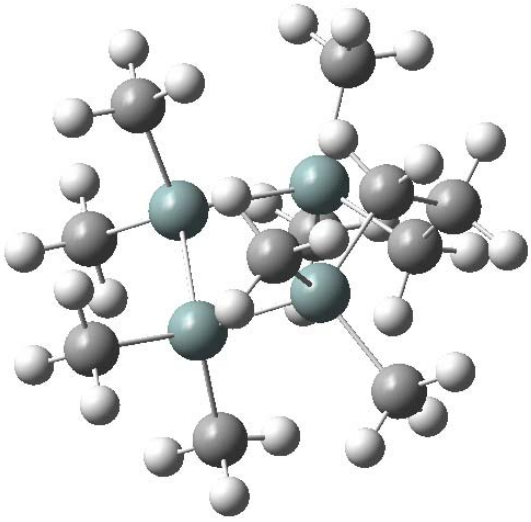
Figure S2. (cont) Structures of *n*-Si_4Me_{10} (**10**) at dihedral angles ω = 0 - 180º



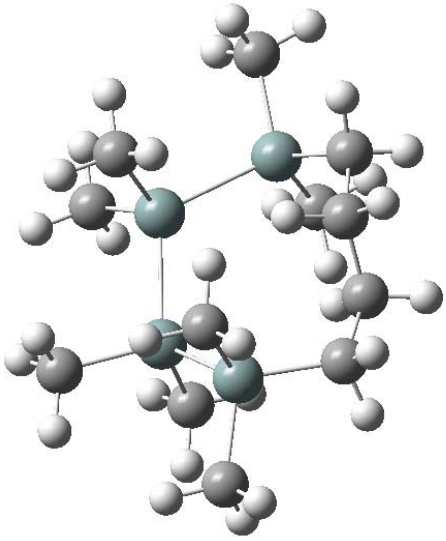
1



2b

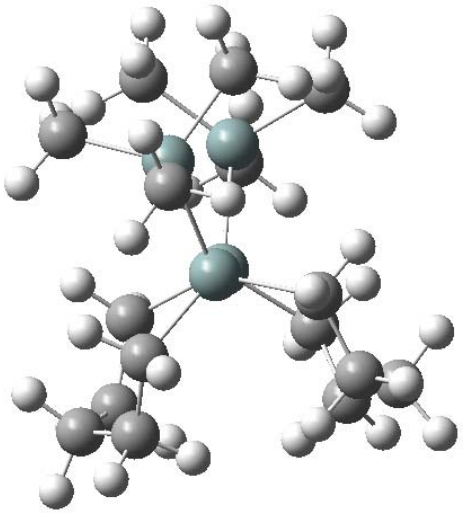


3a

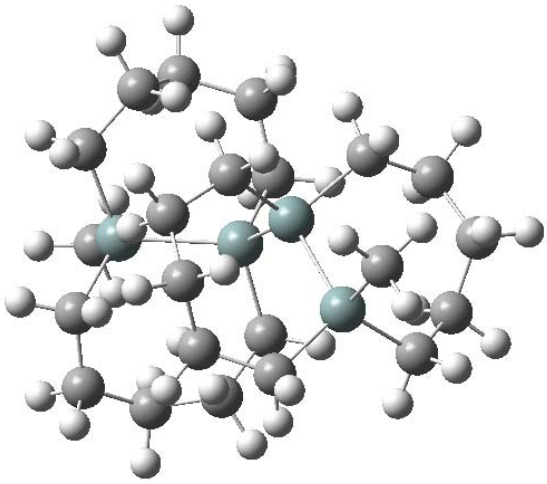


4b

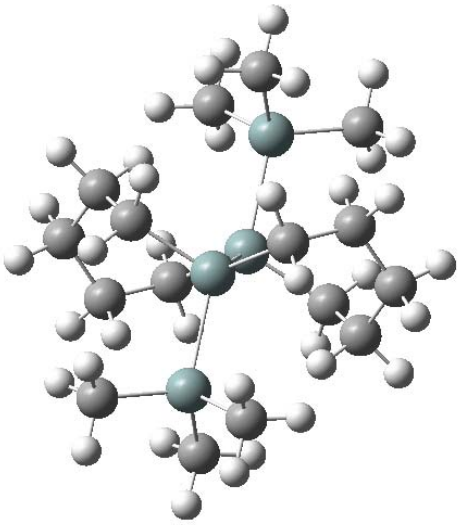
Figure S2. (cont) Structures of **1 - 4** ($Si_4Me_8(CH_2)_n$, n = 1 - 4), and **5 – 7.**



5: ω=23.5º, δ=118.8º (C_2)



6: ω=119.6º, δ=118.2º (C_1)



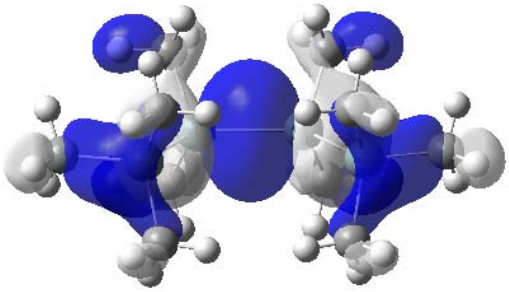
7: ω=180.0º, δ=116.7º (C_{2h})

Figure S2. (cont) Structures of **1 - 4** ($Si_4Me_8(CH_2)_n$, n = 1 - 4), and **5 - 7**

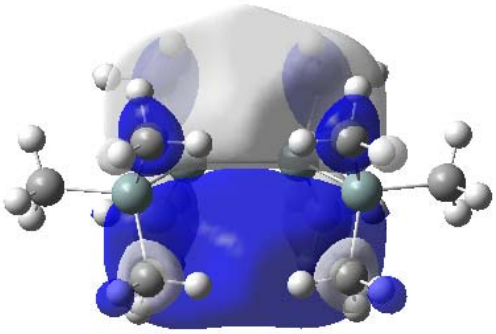
6. MOs of *n*-Si_4Me_{10} (10) Relevant for Low-Lying States with High Intensity

***ω* = 0 °**

$1B_1$ (1B) state

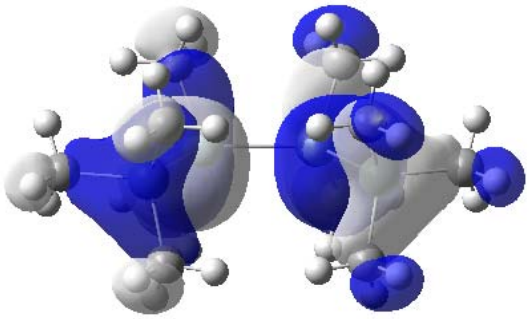


HOMO (a_1, a, σ)

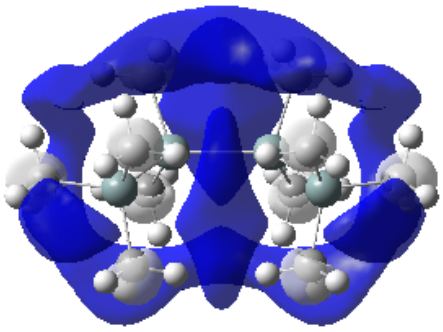


LUMO (b_1, b, π*)

$1B_2$ (2B) state



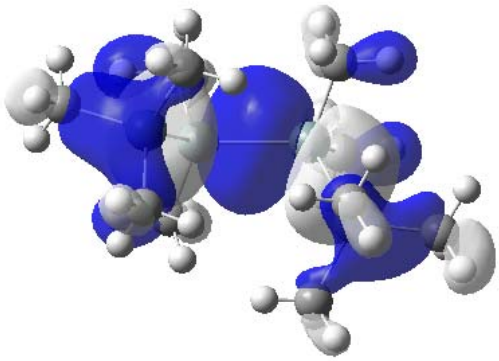
HOMO-1 (b_2, b, σ)



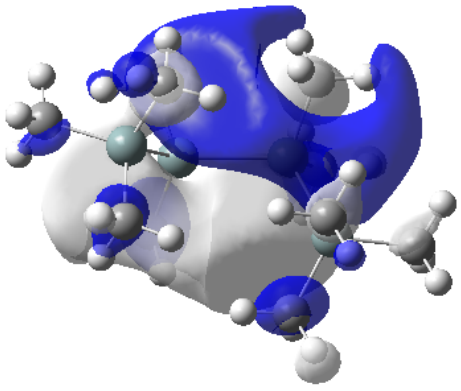
LUMO+1 (a_1, a, σ*)

***ω* = 60 °**

1B state



HOMO (a, σ)

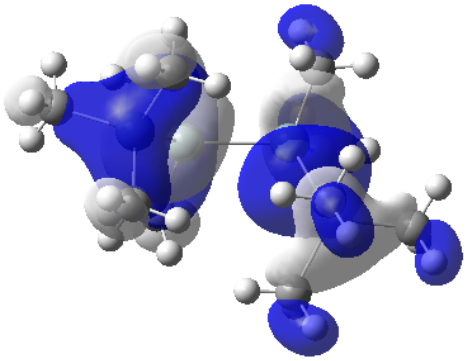


LUMO+1 (b, π*)

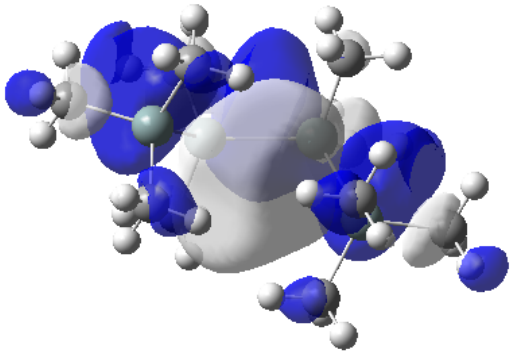
Figure S3. Relevant MOs of *n*-Si_4Me_{10} (**10**)

ω = 60 º

2B state



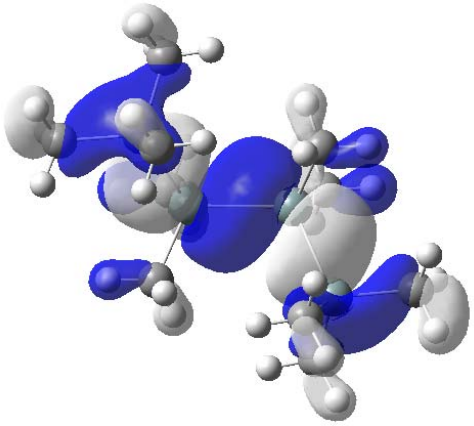
HOMO-1 (b, σ)



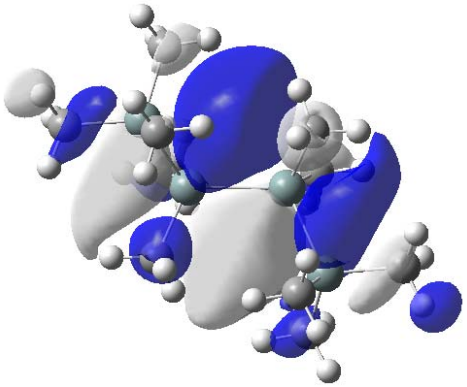
LUMO (a, σ*)

ω = 120 º

1B state

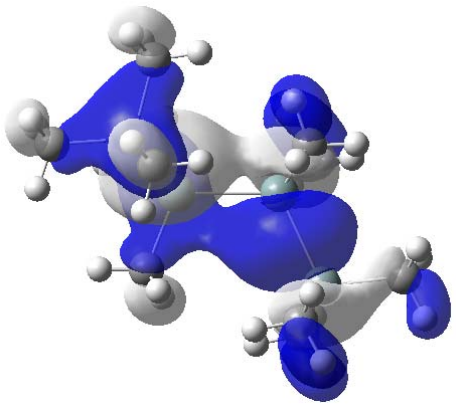


HOMO (a, σ)

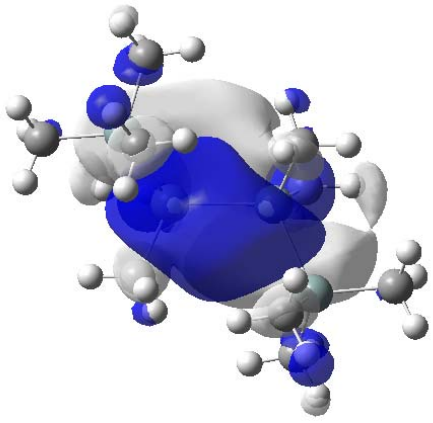


LUMO (b, σ*)

2B state



HOMO-1 (b, σ)

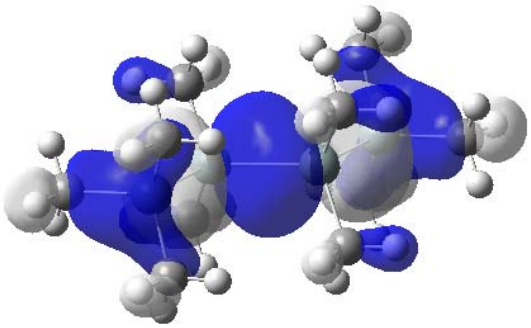


LUMO+1 (a, π*)

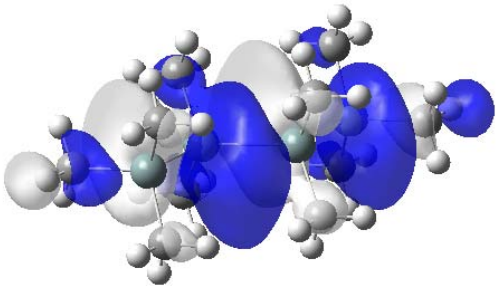
Figure S3. (cont) Relevant MOs of *n*-Si_4Me_{10} (**10**)

ω = 180 º

$1B_u$ (1B) state

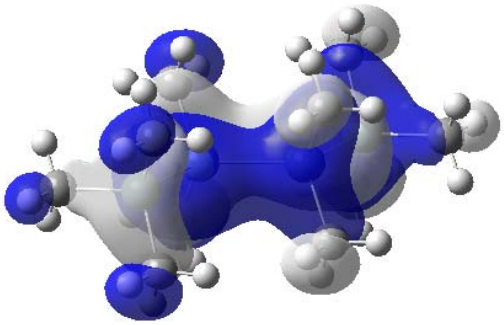


HOMO (a_g, a, σ)

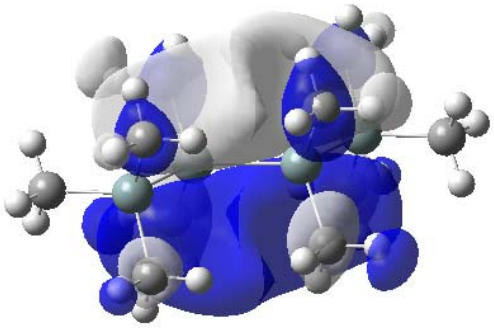


LUMO (b_u, b, σ*)

$2B_g$ (2B) state



HOMO-1 (b_u, b, σ)



LUMO+1 (a_u, a, π*)

Figure S3. (cont) Relevant MOs of *n*-Si_4Me_{10} (**10**)

7. SAC-CI Spectra of *n*-Si_4Me_{10} (10) at Dihedral Angles ω = 0 to 180º

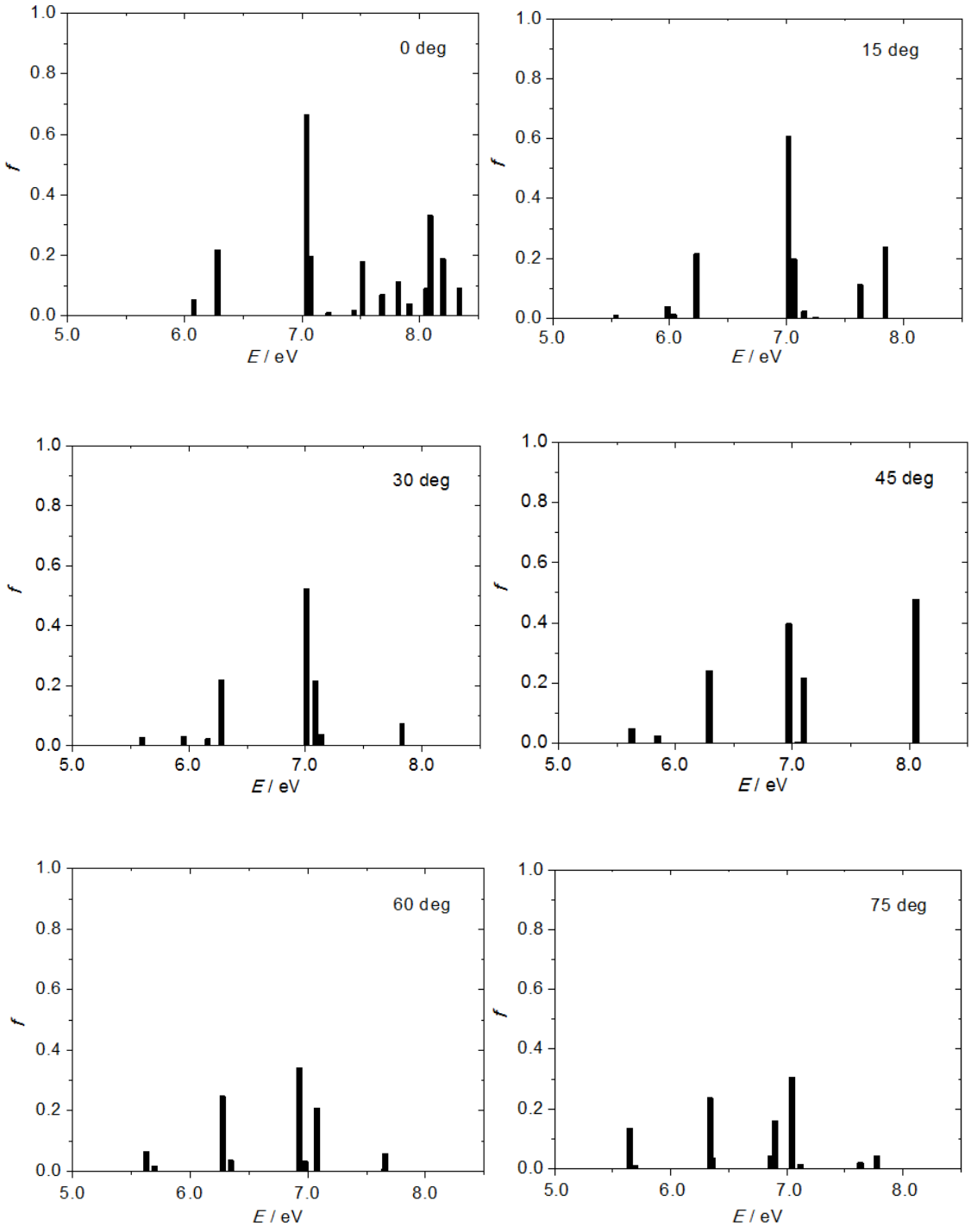


Figure S4. SAC-CI spectra of *n*-Si_4Me_{10} (**10**) at dihedral angles ω = 0 - 180º

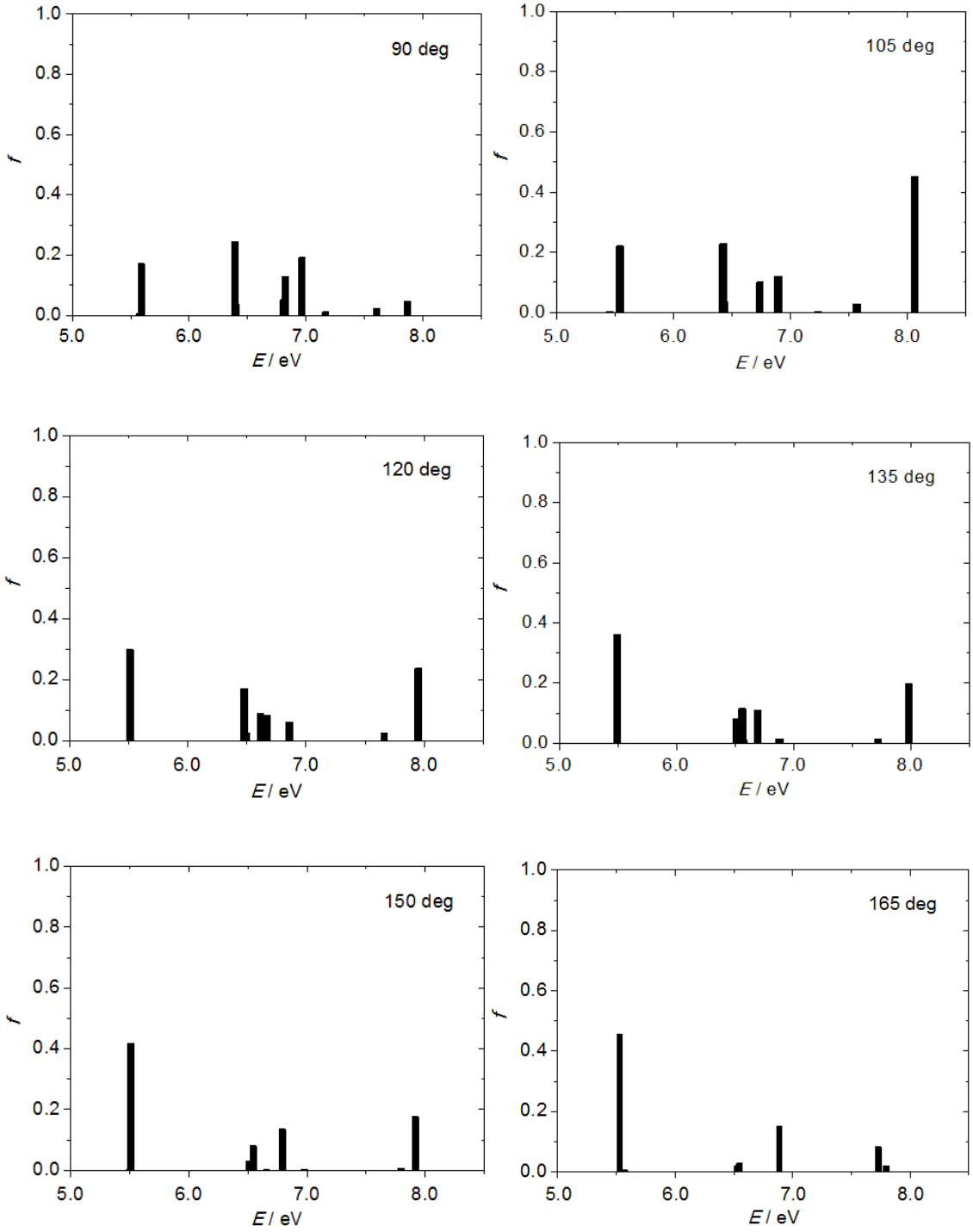


Figure S4. (cont) SAC-CI spectra of *n*-Si_4Me_{10} (**10**) at dihedral angles ω = 0 - 180º

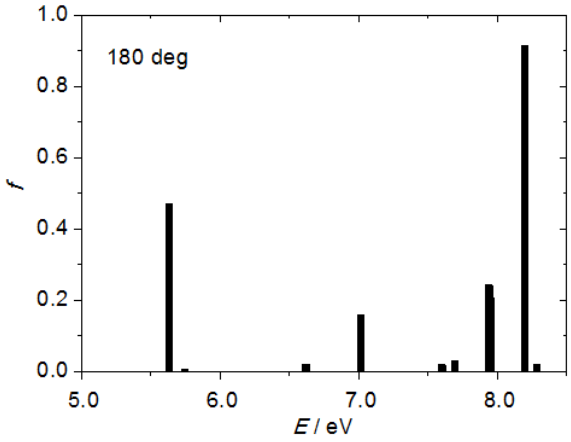


Figure S4. (cont) SAC-CI spectra of *n*-Si_4Me_{10} (**10**) at dihedral angles ω = 0 - 180º.

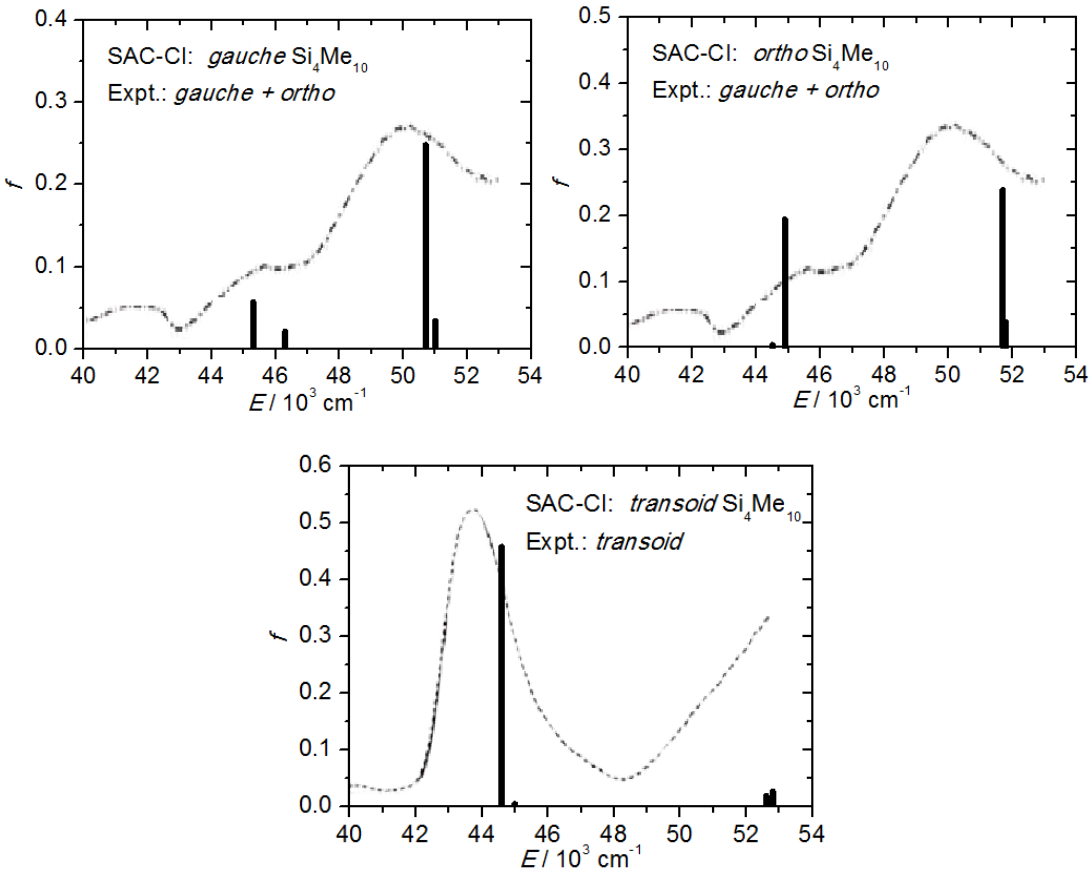
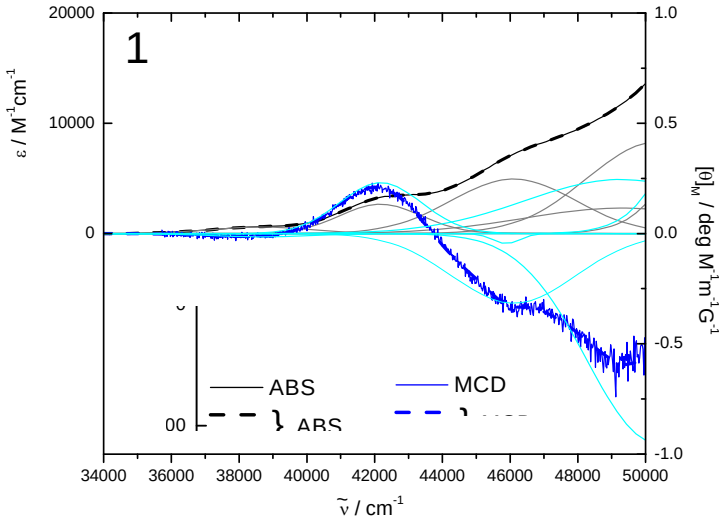
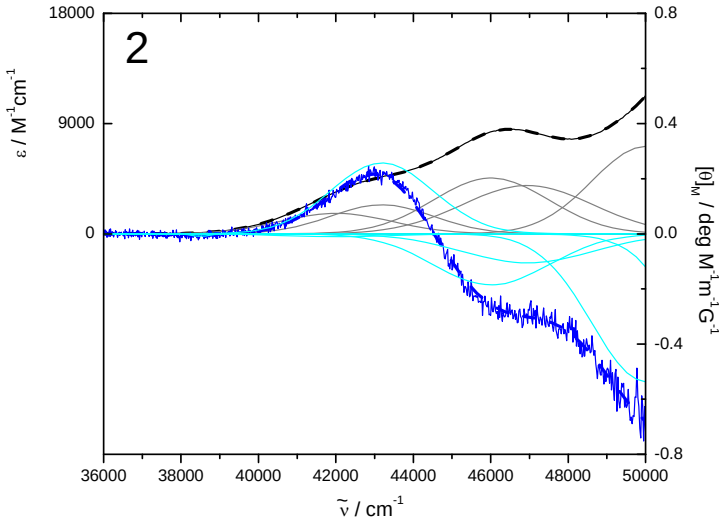
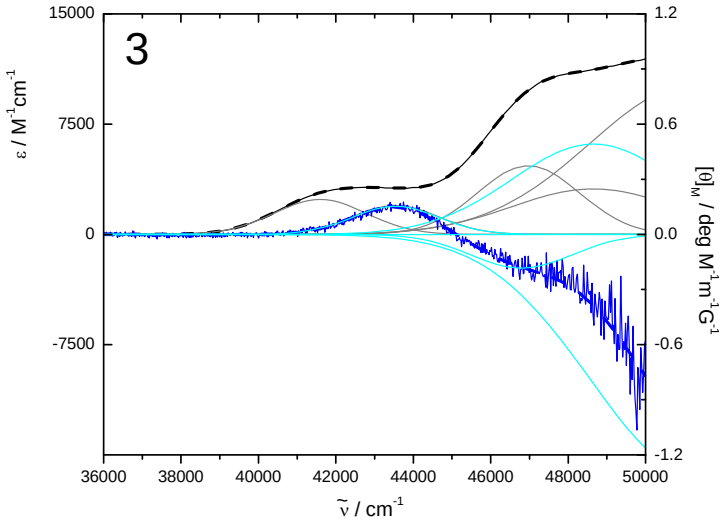


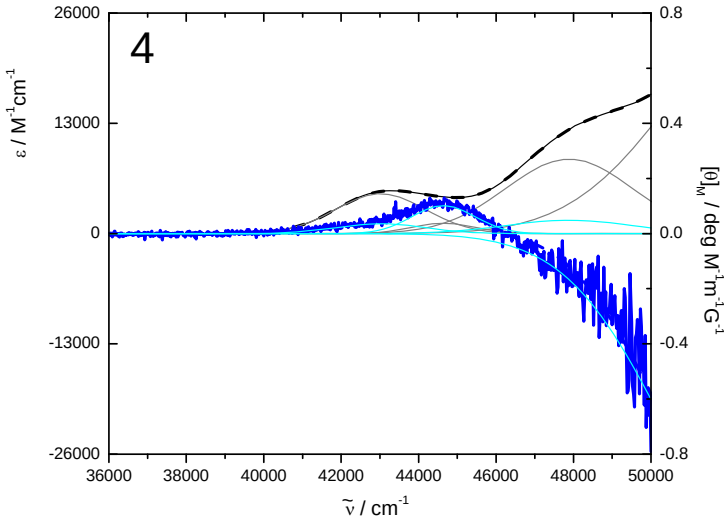
Figure S4. (cont) SAC-CI spectra of *n*-Si_4Me_{10} (**10**) at three local minima compared with experimental spectra, taken from Ref. [45].

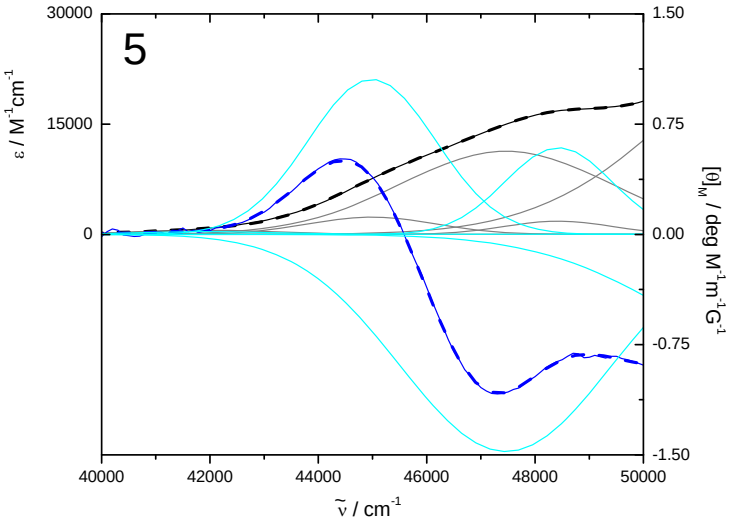
8. Gaussian Fitting of UV Absorption and MCD Spectra

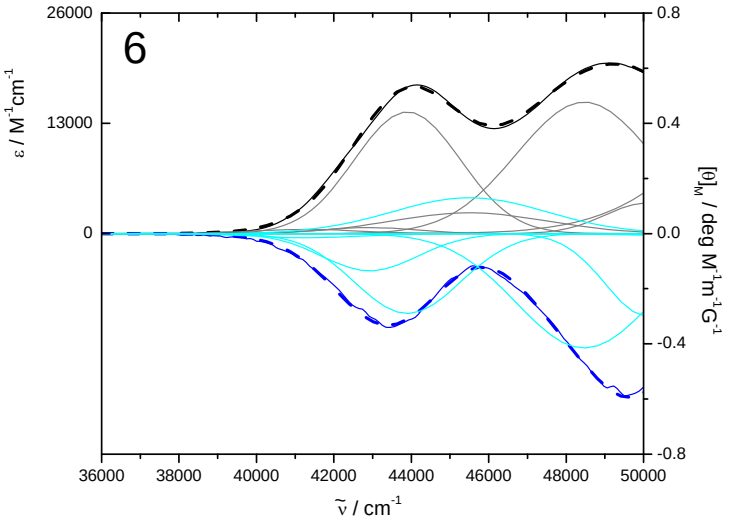


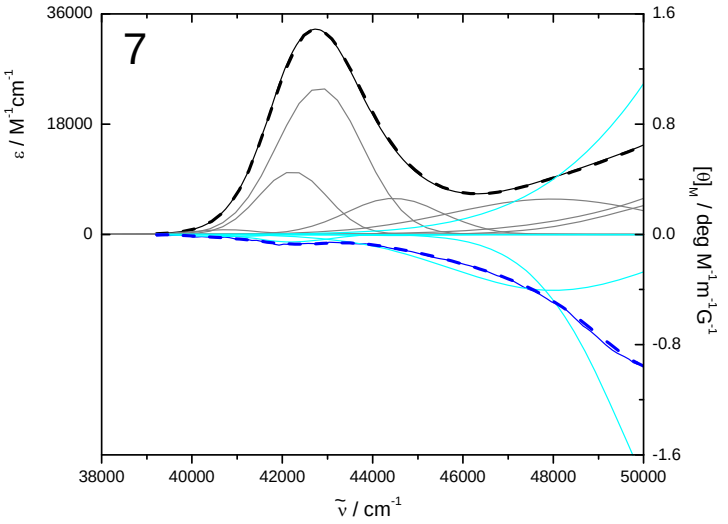


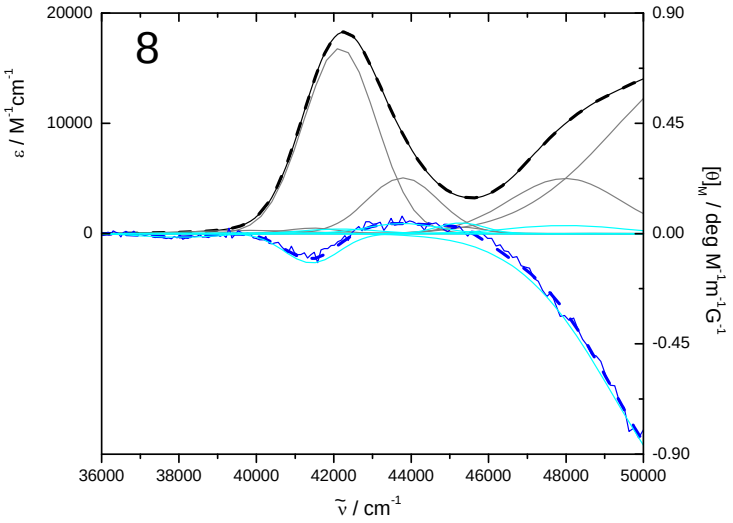

3
15000
7500
0
-7500
1.2
0.6
0.0
-0.6
-1.2
36000
38000
40000
42000
44000
46000
48000
50000
ε / M-1cm-1
[θ]M / deg M-1m-1G-1
ν̃ / cm-1


4
26000
13000
0
-13000
-26000
0.8
0.4
0.0
-0.4
-0.8
36000
38000
40000
42000
44000
46000
48000
50000
ε / M-1cm-1
[θ]M / deg M-1m-1G-1
ν̃ / cm-1


5
30000
15000
0
1.50
0.75
0.00
-0.75
-1.50
40000
42000
44000
46000
48000
50000
ε / M-1cm-1
[θ]M / deg M-1m-1G-1
ν̃ / cm-1


6
26000
13000
0
0.8
0.4
0.0
-0.4
-0.8
36000
38000
40000
42000
44000
46000
48000
50000
ε / M-1cm-1
[θ]M / deg M-1m-1G-1
ν̃ / cm-1


7
36000
18000
0
1.6
0.8
0.0
-0.8
-1.6
38000
40000
42000
44000
46000
48000
50000
ε / M-1cm-1
[θ]M / deg M-1m-1G-1
ν̃ / cm-1


8
20000
10000
0
0.90
0.45
0.00
-0.45
-0.90
36000
38000
40000
42000
44000
46000
48000
50000
ε / M-1cm-1
[θ]M / deg M-1m-1G-1
ν̃ / cm-1

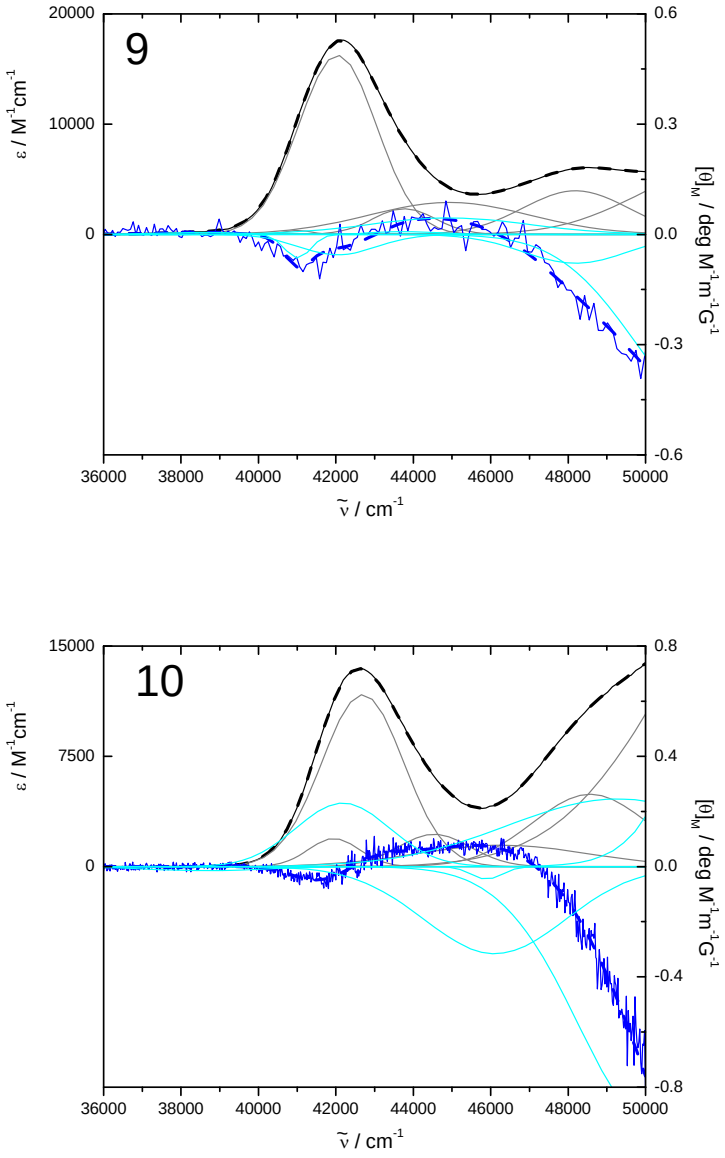


Figure S5. Gaussian fitting of UV absorption and MCD spectra

Table S8. Band center (ν_{max}), full width half maximum (FWHM), and integrated area under the band (A) determined by Gaussian fitting.

	ν_{max}	FWHM	A_{ABS}	A_{MCD}
	10^3 cm^{-1}	10^3 cm^{-1}	10^3 M^{-1} cm^{-2}	deg $M^{-1}G^{-1}10^{-2}cm^{-2}$
1	38.643	1.501	0.585	-0.0147
	42.179	1.209	2.654	0.230
	45.899	0.400	0.0469	-0.0455
	46.103	1.830	4.943	-0.316
	49.273	2.845	2.311	0.245
	50.299	2.028	8.265	-0.947
	55.564	2.098	90.275	6.14
2	38.500	0.218	0.00657	-0.01
	41.997	1.441	1.670	-0.0103
	43.191	1.324	2.372	0.257
	46.012	1.487	4.562	-0.185
	46.951	1.681	3.940	-0.105
	50.016	1.394	7.145	-0.537
	56.095	2.048	270.273	-10.1
3	41.593	1.188	2.370	-0.00174
	43.537	1.120	1.976	0.153
	46.791	1.312	4.676	-0.184
	48.655	2.122	3.095	0.491
	51.287	2.716	10.245	-1.30
4	43.017	1.158	4.699	0.0356
	44.638	0.816	1.220	0.101
	47.888	1.636	8.776	0.0482
	53.016	2.596	24.707	-1.18
5	41.960	1.272	0.558	0.0187
	44.988	1.174	2.333	1.06
	47.464	1.946	11.295	-1.48
	48.434	0.988	1.789	0.590
	53.352	2.627	28.877	-0.937
6	41.295	1.400	0.490	-0.015
	42.928	1.242	0.700	-0.135
	43.900	1.370	14.350	-0.290
	45.500	2.000	2.450	0.130

	48.469	1.750	15.500	-0.415
	50.100	1.089	3.600	-0.30
	55.999	3.088	31.500	-0.0368
7	40.754	0.716	0.761	-0.017
	42.230	0.755	10.248	-0.0554
	42.924	0.954	23.890	-0.00228
	44.473	1.053	5.882	-0.00869
	47.989	2.251	5.766	-0.407
	51.609	1.994	6.532	-2.46
	56.121	3.765	22.026	4.10
8	38.000	0.900	0.0005	-0.015
	39.808	1.400	0.289	0.004
	41.432	0.700	0.488	-0.12
	42.162	0.939	16.821	0.0188
	43.782	0.917	5.052	0.041
	45.286	0.604	0.592	0.044
	47.972	1.427	4.990	0.0332
	51.737	2.488	15.624	-1.10
9	38.495	1.040	0.185	0.00559
	41.012	0.335	0.368	-0.0647
	42.042	1.009	16.243	-0.0551
	43.767	0.806	2.333	0.00772
	44.927	2.065	2.895	0.0446
	48.194	1.357	3.956	-0.0783
	51.724	2.002	5.666	-0.48
10	41.363	0.700	0.017	-0.0396
	41.948	0.661	1.910	-0.0376
	42.693	1.057	11.704	0.0171
	44.540	0.931	2.203	-0.0156
	46.298	2.209	1.456	0.126
	48.568	1.488	4.921	0.0721
	53.688	2.973	22.391	-1.81