Electronic Supplementary Information for Dalton Transactions

The experimental gas-phase structures of 1,3,5-trisilylbenzene and hexasilylbenzene and the theoretical structures of all benzenes with three or more silyl substituents

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Table S1. Computed parameters for the tri-, tetra-, penta- and hexa-silylbenzenes.[a]

Substituent positions	Parameter	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
1,2,3	C(1)-Si(7)	188.8	189.6	189.4	189.0
	C(2)-Si(8)	189.0	189.8	189.4	189.1
	C(4)-H(10)	107.3	107.6	108.9	109.3
	C(5)-H(11)	107.2	107.6	108.8	109.1
	C(1)-C(2)	141.3	141.1	141.9	142.5
	C(1)-C(6)	139.6	139.6	140.4	141.0
	C(5)-C(6)	137.9	138.2	139.0	139.7
	C(1)-C(2)-C(3)	119.6	119.7	119.8	119.7
	C(6)-C(1)-C(2)	119.0	119.0	119.1	119.0
	C(5)-C(6)-C(1)	121.4	121.4	121.3	121.3
	C(4)-C(5)-C(6)	119.6	119.4	119.6	119.6
	Si(7)-C(1)-C(2)	124.8	125.2	124.7	124.6
	Si(7)-C(1)-C(6)	116.2	115.8	116.2	116.4
	Si(8)-C(2)-C(1)	120.2	120.1	120.1	120.1
	H(12)-C(6)-C(1)	119.8	119.9	119.8	119.9
	H(12)-C(6)-C(5)	118.9	118.7	118.9	118.8
	H(11)-C(5)-C(6)	120.2	120.3	120.2	120.2
1,2,4	C(2)-Si(8)	188.6	189.4	189.3	188.9
	C(1)-Si(7)	188.4	189.3	189.0	188.6
	C(6)-H(12)	107.5	107.8	109.1	109.4
	C(5)-H(11)	107.3	107.6	108.9	109.3
	C(4)-Si(10)	187.7	188.5	188.3	188.0
	C(3)-H(9)	107.4	107.7	109.1	109.5
	C(1)-C(2)	141.2	141.1	141.8	142.3
	C(2)-C(3)	139.5	139.4	140.4	141.1
	C(3)-C(4)	139.6	139.7	140.3	140.9
	C(4)-C(5)	139.0	138.9	140.0	140.6
	C(5)-C(6)	138.3	138.6	139.3	139.9
	C(6)-C(1)	139.3	139.2	140.2	140.9
	C(1)-C(2)-C(3)	118.5	118.4	118.5	118.6

	C(2)-C(3)-C(4)	122.9	123.1	122.9	122.9
	C(3)-C(4)-C(5)	117.6	117.4	117.5	117.6
	C(4)-C(5)-C(6)	120.7	120.7	120.7	120.6
	C(5)-C(6)-C(1)	121.7	121.8	121.8	121.8
	C(6)-C(1)-C(2)	118.6	118.6	118.6	118.6
	Si(7)-C(1)-C(2)	125.0	125.2	124.7	125.0
	Si(7)-C(1)-C(6)	116.4	116.2	116.7	116.5
	Si(8)-C(2)-C(3)	117.0	116.7	116.9	117.0
	Si(8)-C(2)-C(1)	124.5	124.8	124.6	124.5
	H(9)-C(3)-C(4)	118.6	118.5	118.7	118.7
	H(9)-C(3)-C(2)	118.6	118.5	118.4	118.4
	Si(10)-C(4)-C(5)	121.4	121.4	121.3	121.5
	Si(10)-C(4)-C(3)	121.0	121.2	121.2	121.0
	H(11)-C(5)-C(6)	119.1	119.0	119.1	119.1
	H(11)-C(5)-C(4)	120.2	120.3	120.3	120.3
	H(12)-C(6)-C(1)	119.8	119.9	119.9	119.9
	H(12)-C(6)-C(5)	118.5	118.3	118.3	118.3
1,3,5	C(1)-Si(7)	187.6	188.3	188.3	188.0
	C(2)-H(10)	107.5	107.8	109.1	109.5
	C(1)-C(2)	139.8	140.0	140.6	141.1
	C(2)-C(3)	139.0	138.9	140.0	140.7
	C(2)-C(3)-C(4)	117.9	117.7	117.9	118.0
	C(1)-C(2)-C(3)	122.2	122.3	122.1	122.0
	Si(7)-C(1)-C(2)	120.9	121.1	121.1	120.9
	Si(7)-C(1)-C(6)	121.3	121.2	121.0	121.2
	H(10)-C(2)-C(3)	118.9	118.8	118.8	118.8
	H(10)-C(2)-C(1)	119.0	118.9	119.1	119.2
1,2,3,4	C(1)-Si(7)	189.1	189.9	189.5	189.4
	C(2)-Si(8)	189.4	190.2	189.8	189.8
	C(5)-H(11)	107.3	107.6	108.8	108.9
	C(1)-C(2)	141.5	141.4	142.2	142.2
	C(2)-C(3)	141.3	141.0	142.1	142.3
	C(1)-C(6)	139.1	139.0	140.3	140.4

	C(5)-C(6)	137.9	138.3	139.2	139.3
	C(1)-C(2)-C(3)	120.0	120.1	120.1	120.1
	C(3)-C(4)-C(5)	118.6	118.6	118.6	118.6
	C(4)-C(5)-C(6)	121.4	121.3	121.3	121.2
	Si(7)-C(1)-C(2)	125.6	126.0	125.5	125.6
	Si(7)-C(1)-C(6)	115.8	115.5	115.9	115.8
	Si(8)-C(2)-C(3)	120.9	121.0	120.7	120.8
	Si(8)-C(2)-C(1)	119.1	118.9	119.2	119.0
	H(11)-C(5)-C(6)	118.6	118.5	118.8	118.8
	H(11)-C(5)-C(4)	120.0	120.2	119.9	120.0
1,2,3,5	C(1)-Si(7)	188.9	189.7	189.4	189.3
	C(2)-Si(8)	189.2	190.0	189.4	189.4
	C(4)-H(10)	107.4	107.7	108.9	109.1
	C(5)-Si(11)	187.8	188.5	188.3	188.2
	C(1)-C(2)	141.2	141.0	142.0	142.1
	C(1)-C(6)	139.5	139.6	140.6	140.7
	C(4)-C(5)	139.0	139.1	140.2	140.3
	C(1)-C(2)-C(3)	119.5	119.6	119.5	119.5
	C(2)-C(3)-C(4)	119.0	118.9	119.1	119.1
	C(3)-C(4)-C(5)	122.5	122.7	122.5	122.4
	C(4)-C(5)-C(6)	117.5	117.2	117.4	117.5
	Si(7)-C(1)-C(2)	124.8	125.2	124.6	124.8
	Si(7)-C(1)-C(6)	116.2	115.9	116.3	116.1
	Si(8)-C(2)-C(1)	120.3	120.2	120.2	120.2
	H(10)-C(4)-C(3)	118.7	118.7	118.7	118.7
	H(10)-C(4)-C(5)	118.7	118.6	118.9	118.8
	H(11)-C(5)-C(4)	121.3	121.4	121.3	121.3
1,2,4,5	C(1)-Si(7)	188.5	189.3	188.9	188.8
	C(3)-H(9)	107.4	107.7	108.9	109.1
	C(2)-C(3)	139.4	139.5	140.5	140.6
	C(1)-C(2)	140.7	140.5	141.6	141.7
	C(1)-C(2)-C(3)	118.4	118.4	118.4	118.5
	C(2)-C(3)-C(4)	123.1	123.3	123.2	123.0

	Si(7)-C(1)-C(2)	123.7	124.1	123.7	123.7
	Si(7)-C(1)-C(6)	117.8	117.5	117.8	117.8
	H(9)-C(3)-C(2)	118.5	118.4	118.4	118.5
1,2,3,4,5	C(1)-Si(7)	189.2	190.0	189.6	189.5
	C(2)-Si(8)	189.7	190.5	190.0	189.9
	C(3)-Si(9)	189.8	190.6	190.1	190.2
	C(6)-H(12)	107.3	107.6	108.8	109.0
	C(1)-C(2)	140.9	140.7	141.8	141.9
	C(2)-C(3)	141.4	141.2	142.2	142.3
	C(1)-C(6)	139.2	139.2	140.3	140.4
	C(1)-C(2)-C(3)	119.6	119.68	119.65	119.67
	C(2)-C(3)-C(4)	120.4	120.5	120.5	120.5
	C(5)-C(6)-C(1)	123.1	123.2	123.1	122.9
	C(6)-C(1)-C(2)	118.6	118.4	118.5	118.5
	C(1)-C(2)-C(3)	119.6	119.7	119.7	119.7
	Si(7)-C(1)-C(2)	125.6	126.1	125.6	125.6
	Si(7)-C(1)-C(6)	115.0	115.5	115.9	115.9
	Si(8)-C(2)-C(1)	119.0	118.8	119.0	118.9
	Si(8)-C(2)-C(3)	121.4	121.5	121.3	121.3
	Si(9)-C(3)-C(2)	119.8	119.7	119.7	119.6
	H(12)-C(6)-C(1)	118.4	118.4	118.5	118.6
1,2,3,4,5,6	C-Si	190.2	191.0	190.5	190.5
	C-C	141.1	140.9	141.9	142.0
	C(1)-C(2)-C(3)	119.98	119.99	119.99	120.00

[a] Distances in pm, angles in degrees.

Table S2. Angles between C-Si or C-H bonds and the planes defined by the adjacent ring C-C bonds, calculated *ab initio* for the tri-, tetra-, penta- and hexa-silylbenzenes.[a]

Substituent positions	Carbon atom	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
1,2,3	C(1)	0.3	0.5	0.2	2.1
	C(2)	-0.4	-0.3	-0.4	-2.0
	C(3)	0.3	0.5	0.2	2.1
	C(4)	-0.3	-0.2	0.3	-2.7
	C(5)	0.2	0.2	-0.2	0.9
	C(6)	-0.3	-0.2	0.3	-2.7
1,2,4	C(1)	-0.8	-0.8	-0.8	-1.6
	C(2)	0.5	0.4	0.3	0.8
	C(3)	-0.1	-0.2	-0.3	-0.9
	C(4)	0.0	0.3	0.7	1.3
	C(5)	0.0	-0.1	-0.2	-0.6
	C(6)	0.2	0.0	-0.1	0.3
1,3,5	All	0.0	0.0	0.0	0.0
1,2,3,4	C(1)	-0.3	-0.9	-0.2	-1.4
	C(2)	1.1	1.6	1.2	2.2
	C(3)	-1.1	-1.6	-1.2	-2.2
	C(4)	0.3	0.9	0.2	1.4
	C(5)	-0.2	-0.4	-0.3	-0.7
	C(6)	0.2	0.4	0.3	0.7
1,2,3,5	C(1)	0.5	0.6	0.6	0.6
	C(2)	-0.5	-0.4	-0.4	-0.7
	C(3)	0.5	0.6	0.6	0.6
	C(4)	-0.5	-0.4	-0.4	-0.7
	C(5)	0.2	0.1	0.2	0.3
	C(6)	-0.5	-0.4	-0.4	-0.7
1,2,4,5	C(1)	0.7	0.6	0.7	1.2
	C(2)	-0.7	-0.6	-0.7	-1.2
	C(3)	0.2	0.1	0.1	0.4
	C(4)	-0.7	-0.6	-0.7	-1.2

	C(5)	0.7	0.6	0.7	1.2
	C(6)	-0.2	-0.1	-0.1	-0.4
1,2,3,4,5	C(1)	1.2	1.5	1.3	2.6
	C(2)	-1.2	-2.8	-2.3	-4.0
	C(3)	2.2	2.7	2.2	3.9
	C(4)	-1.2	-2.8	-2.3	-4.0
	C(5)	1.2	1.5	1.3	2.6
	C(6)	-0.4	-0.6	-0.5	-1.3
1,2,3,4,5,6	All	4.1	4.7	4.4	6.6

[a] Angles in degrees.

Table S3. Geometric coordinates for the molecular structures of 1,2,3-tri-silylbenzene, 1,2,4-tri-silylbenzene and 1,3,5-tri-silylbenzene at the MP2 level with a 6-31G* basis set on H and 6-311G* basis set on C and Si. Geometric coordinates for the molecular structures of 1,2,3,4-tetra-silylbenzene, 1,2,3,5-tetra-silylbenzene, 1,2,4,5-tetra-silylbenzene, penta-silylbenzene and hexa-silylbenzene at the MP2 level with the 6-31G* basis set on all atoms.

1,2,3-tri-silylbenzene	*x*	*y*	*z*
C(1)	0.0000	0.2492	0.0000
Si(2)	0.2333	2.1256	0.0000
C(3)	-0.3090	-2.5619	0.0000
H(4)	1.6699	2.4923	0.0000
C(5)	-0.0487	-0.4647	1.2324
C(6)	-0.0487	-0.4647	-1.2324
C(7)	-0.2334	-1.8627	1.2070
C(8)	-0.2334	-1.8627	-1.2070
H(9)	-0.4527	-3.6438	0.0000
H(10)	-0.2744	-2.4239	-2.1435
H(11)	-0.2744	-2.4239	2.1435
Si(12)	0.0563	0.3372	-2.9408
Si(13)	0.0563	0.3372	2.9408
H(14)	-0.4069	2.7055	-1.2031
H(15)	-0.4069	2.7055	1.2031
H(16)	1.1977	1.2798	-3.0159
H(17)	1.1977	1.2798	3.0159
H(18)	0.2574	-0.7550	-3.9230
H(19)	0.2574	-0.7550	3.9230
H(20)	-1.1838	1.0717	-3.2838
H(21)	-1.1838	1.0717	3.2838
Energy	-1102.0718		
1,2,4-tri-silylbenzene	*x*	*y*	*z*
C(1)	-0.5507	0.6140	-0.0108
C(2)	-1.0187	-0.7263	0.0130
C(3)	-0.0752	-1.7685	0.0202
C(4)	1.2968	-1.5110	0.0064
C(5)	1.7806	-0.1941	-0.0169
C(6)	0.8356	0.8475	-0.0277
Si(7)	-1.6914	2.1175	0.0129
Si(8)	-2.8468	-1.1940	-0.0100
H(9)	-0.4133	-2.8039	0.0411
H(10)	1.9915	-2.3504	0.0043
Si(11)	3.6259	0.1699	0.0033
H(12)	1.1920	1.8777	-0.0651
H(13)	-0.8894	3.3034	-0.3837
H(14)	-2.8171	1.9406	-0.9414
H(15)	-2.2613	2.3537	1.3659

H(16)	-3.6169	-0.3538	0.9437
H(17)	-3.4402	-1.0258	-1.3630
H(18)	-2.9567	-2.6212	0.3879
H(19)	4.3540	-0.9468	-0.6530
H(20)	3.8857	1.4398	-0.7226
H(21)	4.1341	0.3102	1.3941
Energy	-1101.9295		
1,3,5-tri-silylbenzene	*x*	*y*	*z*
C(1)	1.2309	0.7134	0.0000
C(2)	-1.2333	0.7093	0.0000
C(3)	0.0024	-1.4227	0.0000
C(4)	0.0000	1.3942	0.0000
C(5)	-1.2074	-0.6971	0.0000
C(6)	1.2074	-0.6971	0.0000
Si(7)	2.8609	1.6509	0.0000
Si(8)	-2.8602	1.6521	0.0000
Si(9)	-0.0007	-3.3030	0.0000
H(10)	0.0020	2.4891	0.0000
H(11)	-2.1566	-1.2428	0.0000
H(12)	2.1546	-1.2463	0.0000
H(13)	2.5730	3.1050	0.0000
H(14)	-3.9756	0.6758	0.0000
H(15)	1.4025	-3.7808	0.0000
H(16)	3.6567	1.3037	1.2012
H(17)	-2.9573	2.5149	1.2012
H(18)	-0.6993	-3.8186	1.2012
H(19)	3.6567	1.3037	-1.2012
H(20)	-2.9573	2.5149	-1.2012
H(21)	-0.6993	-3.8186	-1.2012
Energy	-1102.0765		
1,2,3,4-tetra-silylbenzene	*x*	*y*	*z*
C(1)	-0.2003	0.6826	0.3885
C(2)	0.2003	-0.6826	0.3885
C(3)	-0.3766	1.3744	-0.8414
C(4)	0.3766	-1.3744	-0.8414
C(5)	-0.1699	0.6754	-2.0418
C(6)	0.1699	-0.6754	-2.0418
Si(7)	-0.5663	1.5890	2.0150
Si(8)	0.5663	-1.5890	2.0150
Si(9)	-0.8359	3.2031	-1.0214
Si(10)	0.8359	-3.2031	-1.0214
H(11)	-0.2864	1.1862	-2.9966
H(12)	0.2864	-1.1862	-2.9966
H(13)	-1.5319	2.6817	1.7422
H(14)	1.5319	-2.6817	1.7422
H(15)	-1.1950	0.6561	2.9838

H(16)	1.1950	-0.6561	2.9838
H(17)	0.6547	2.1733	2.6297
H(18)	-0.6547	-2.1733	2.6297
H(19)	-2.2674	3.4639	-0.7210
H(20)	2.2674	-3.4639	-0.7210
H(21)	0.0000	4.0600	-0.1415
H(22)	0.0000	-4.0600	-0.1415
H(23)	-0.5732	3.5640	-2.4387
H(24)	0.5732	-3.5640	-2.4387
Energy	-1392.0797		
1,2,3,5-tetra-silylbenzene	*x*	*y*	*z*
C(1)	0.0000	0.9501	0.0000
C(2)	-0.0291	-1.8998	0.0000
C(3)	0.0024	0.2347	1.2275
C(4)	0.0024	0.2347	-1.2275
C(5)	-0.0097	-1.1719	1.1991
C(6)	-0.0097	-1.1719	-1.1991
Si(7)	0.0246	2.8435	0.0000
Si(8)	-0.0936	-3.7808	0.0000
Si(9)	0.0401	1.0333	2.9436
Si(10)	0.0401	1.0333	-2.9436
H(11)	0.0082	-1.7161	2.1441
H(12)	0.0082	-1.7161	-2.1441
H(13)	1.4137	3.3752	0.0000
H(14)	-1.4978	-4.2702	0.0000
H(15)	-0.6797	3.3510	-1.2038
H(16)	-0.6797	3.3510	1.2038
H(17)	0.5861	-4.2941	-1.2171
H(18)	0.5861	-4.2941	1.2171
H(19)	1.0996	2.0716	3.0297
H(20)	1.0996	2.0716	-3.0297
H(21)	-1.2613	1.6529	3.3047
H(22)	-1.2613	1.6529	-3.3047
H(23)	0.3414	-0.0496	3.9151
H(24)	0.3414	-0.0496	-3.9151
Energy	-1392.0841		
1,2,4,5-tetra-silylbenzene	*x*	*y*	*z*
C(1)	1.3784	-0.0048	-0.0449
C(2)	-1.3784	0.0048	0.0449
C(3)	0.7038	-1.2386	-0.0260
C(4)	-0.7038	1.2386	0.0260
C(5)	-0.7124	-1.2337	0.0222
C(6)	0.7124	1.2337	-0.0222
H(7)	2.4688	-0.0086	-0.0675
H(8)	-2.4688	0.0086	0.0675
Si(9)	1.7439	-2.8129	-0.1008

Si(10)	-1.7439	2.8129	0.1008
Si(11)	-1.7636	-2.8008	0.0923
Si(12)	1.7636	2.8008	-0.0923
H(13)	3.1448	-2.4482	0.2320
H(14)	-3.1448	2.4482	-0.2320
H(15)	1.2463	-3.8161	0.8760
H(16)	-1.2463	3.8161	-0.8760
H(17)	1.7132	-3.4240	-1.4558
H(18)	-1.7132	3.4240	1.4558
H(19)	-3.1619	-2.4253	-0.2394
H(20)	3.1619	2.4253	0.2394
H(21)	-1.2731	-3.8046	-0.8876
H(22)	1.2731	3.8046	0.8876
H(23)	-1.7372	-3.4163	1.4454
H(24)	1.7372	3.4163	-1.4454
Energy	-1392.0859		
penta-silylbenzene	*x*	*y*	*z*
C(1)	0.0300	1.0176	0.0000
C(2)	-0.0065	0.3121	1.2350
C(3)	-0.0065	0.3121	-1.2350
C(4)	-0.0065	-1.1066	1.2335
C(5)	-0.0065	-1.1066	-1.2335
C(6)	0.0414	-1.7763	0.0000
Si(7)	0.3034	2.8995	0.0000
Si(8)	-0.1721	1.2291	2.8898
Si(9)	-0.1721	1.2291	-2.8898
Si(10)	0.0097	-2.2102	2.7738
Si(11)	0.0097	-2.2102	-2.7738
H(12)	0.0956	-2.8650	0.0000
H(13)	-0.9602	3.6818	0.0000
H(14)	1.1004	3.2652	1.1974
H(15)	1.1004	3.2652	-1.1974
H(16)	-0.9870	2.4564	2.7073
H(17)	-0.9870	2.4564	-2.7073
H(18)	-0.8888	0.3413	3.8385
H(19)	-0.8888	0.3413	-3.8385
H(20)	1.1409	1.5986	3.4802
H(21)	1.1409	1.5986	-3.4802
H(22)	-1.3236	-2.2948	3.4235
H(23)	-1.3236	-2.2948	-3.4235
H(24)	0.4057	-3.5666	2.3152
H(25)	0.4057	-3.5666	-2.3152
H(26)	0.9985	-1.7269	3.7717
H(27)	0.9985	-1.7269	-3.7717
Energy	-1682.2337		
hexa-silylbenzene	*x*	*y*	*z*

C(1)	0.0000	1.4204	0.0035
C(2)	1.2301	-0.7102	0.0035
C(3)	-1.2301	-0.7102	0.0035
C(4)	-1.2301	0.7102	-0.0035
C(5)	0.0000	-1.4204	-0.0035
C(6)	1.2301	0.7102	-0.0035
Si(7)	0.0000	3.3041	-0.2779
Si(8)	2.8615	-1.6521	-0.2779
Si(9)	-2.8615	-1.6521	-0.2779
Si(10)	-2.8615	1.6521	0.2779
Si(11)	0.0000	-3.3041	0.2779
Si(12)	2.8615	1.6521	0.2779
H(13)	0.0000	4.1047	0.9735
H(14)	3.5548	-2.0523	0.9735
H(15)	-3.5548	-2.0523	0.9735
H(16)	-3.5548	2.0523	-0.9735
H(17)	0.0000	-4.1047	-0.9735
H(18)	3.5548	2.0523	-0.9735
H(19)	1.1970	3.6560	-1.0821
H(20)	-1.1970	3.6560	-1.0821
H(21)	2.5676	-2.8647	-1.0821
H(22)	3.7647	-0.7913	-1.0821
H(23)	-3.7647	-0.7913	-1.0821
H(24)	-2.5676	-2.8647	-1.0821
H(25)	-3.7647	0.7913	1.0821
H(26)	-2.5676	2.8647	1.0821
H(27)	1.1970	-3.6560	1.0821
H(28)	-1.1970	-3.6560	1.0821
H(29)	2.5676	2.8647	1.0821
H(30)	3.7647	0.7913	1.0821
Energy	-1972.3798		

Figure S1. Molecular scattering intensity and final weighted difference curves for 1,3,5-trisilylbenzene. (a) Long camera distance. (b) Short camera distance.

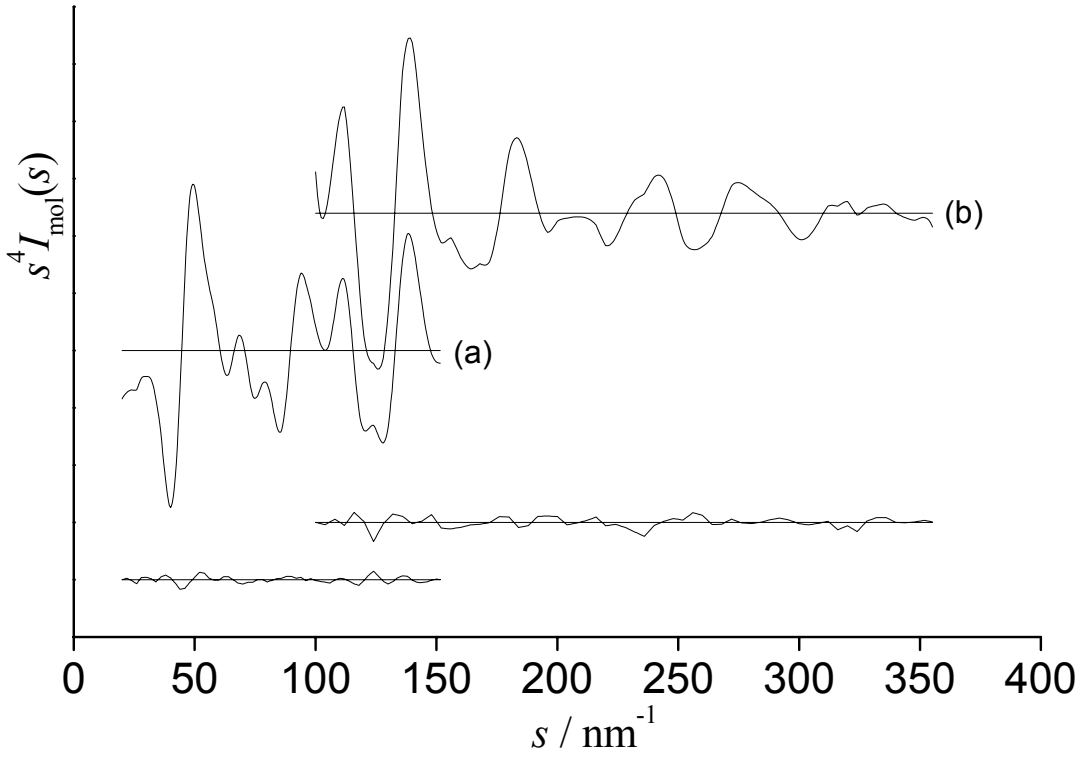

Figure S2. Molecular scattering intensity and final weighted difference curves for hexasilylbenzene. (a) Long camera distance. (b) Short camera distance.