Electronic Supplementary Material (ESI) for Dalton Transactions

Silanetriols in the gas phase: single molecules vs. hydrogen-bonded dimers

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Experimental

Silanetriol **1** was synthesized according to a published literature procedure.[1] The purity of the sample was checked by ^{1}H, ^{13}C and ^{29}Si-NMR spectroscopy prior to gas electron diffraction. The electron diffraction intensities were recorded with a modified Balzers Eldigraph KD-G2 using an electron acceleration voltage of 60 kV.[2] The data were recorded at nozzle-to-plate distances of 250.0 and 500.0 mm, respectively. For each nozzle to plate distance, the electron wavelength was calibrated by reference measurements of benzene at room temperature. The sample was held at 150±5°C during the experiment while the nozzle was kept at 163±5°C The primary beam current was about 380 nA. During data acquisition the pressure rose from $1 \cdot 10^{-6}$ mbar (background pressure) to $1 \cdot 10^{-5}$ mbar. The optimal exposure time was 30 s. The imaging plates (Fuji BAS-IP MP 2025) were analyzed by established procedures using the program XPIMAG. The averaged molecular intensities in the *s* ranges of 3.0 to 12.8 and 6.0 to 28.0 Å are presented in Fig. S1. Table S1 gives further experimental details about the used datasets. For the structure refinement, the program Ed@ed version 2.4[3] and the scattering factors of Ross et al. were used.[4]

Computations

Calculations were carried out with the TURBOMOLE program package (RI-MP2), version 5.10[5] and Gaussian03[6] (B3LYP/6-31g*, HF/6-31g*, MP2/6-31g*, B3LYP/6-31++g**). In case of Turbomole, the calculation for the computational level termed MP2, was performed using the RI-MP2 routine as it is implemented in the ricc2 program deck. TURBOMOLE's def2-TZVPP basis set was used throughout in connection with the corresponding auxiliary basis sets for the RI fit. For the calculations of dimers, the basis set 6-31++g** was chosen. The choice of this basis set was based on the consideration that in order to obtain reliable properties for hydrogen-bonded systems, it is essential to employ a basis set that possesses sufficient diffuseness and angular flexibility. The suitability of this basis set for the calculation of hydrogen bonded complexes has been demonstrated by Dhkissi and coworkers.[7] The program SHRINK was used to compute anharmonic distance corrections and perpendicular curvilinear distance corrections *k*, which in turn were applied in the refinement to yield a r_h type structure.[8]

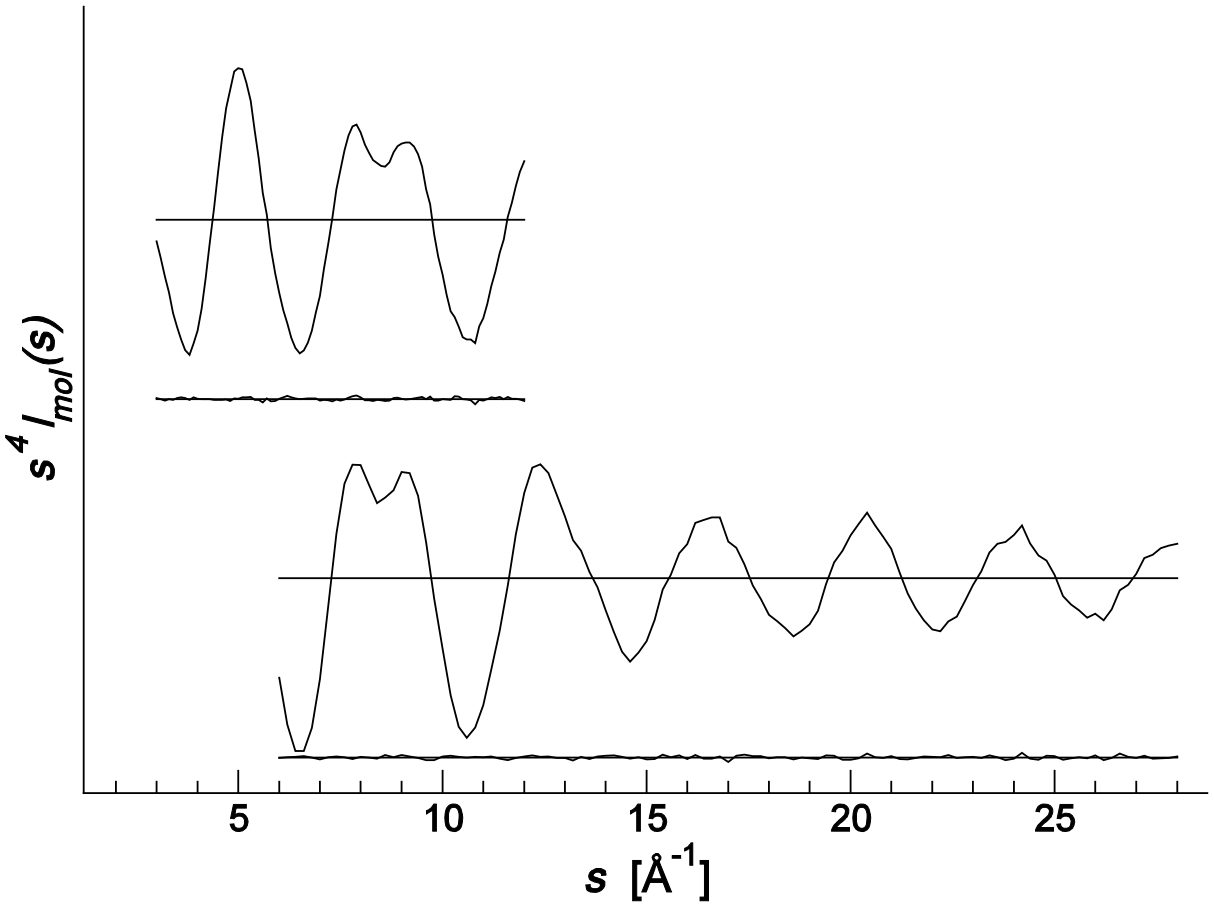


Fig. S1. Experimental and difference (experimental minus theoretical) molecular intensity curves for **1** at nozzle-to-plate distances of 500.0 mm and 250.0 mm, respectively.

Table S1. Summary of the experimental details.

Dataset	R_g %	R_d %	k	e.s.d	Corr. Parameter	Δs (nm^{-1})	s_{min} (nm^{-1})	$sw1$ (nm^{-1})	$sw2$ (nm^{-1})	s_{max} (nm^{-1})	d (mm)	λ (nm)
1	5.09	5.13	0.6931	0.0075	-0.0066	2.00	60.00	80.00	240.0	280.0	250.0	0.04814
2	5.68	3.65	0.7816	0.0081	0.3686	1.00	30.00	40.00	112.0	120.0	500.0	0.04815

Table S2. Comparison of computed and experimental (GED and XRD) data obtained for **1**. Bond lengths in Å and angles in °.

	GED /r_{h1}	B3LYP 6-31g*	HF 6-31g*	MP2 6-31g*	B3LYP 6-31++g**	RIMP2 TZVPP	XRD[1]	XRD[9]	XRD[10]
Si-C	1.879(3)	1.881	1.877	1.865	1.884	1.864	1.865(6)	1.863(2)	1.851(4)-1.871(4)
Si-O	1.640(1)	1.667	1.645	1.670	1.688	1.651	1.613(3)-1.636(4)	1.635(1), 1.640(1)	1.617(2)-1.638(2)
C-C	1.540(2)	1.544	1.541	1.534	1.546	1.532	1.507(6)-1.519(8)	1.536(2), 1.539(3)	1.521(5)-1.534(5)
C-Si-O	111.2(2)	110.5	110.7	110.2	110.3	109.7	109.8(2)-112.3(2)	110.8(5), 111.0(8)	110.2(1)-111.2(2)
C-C-Si	110.5(3)	109.3	109.6	109.3	109.4	109.7	109.0(4)-109.9(4)	109.4(1), 109.8(1)	109.1(2)-110.5(3)
C-H	1.118(2)	1.090	1.086	1.095	1.096	1.090	0.96	1.01(1)	0.98
O-H	0.940(4)	0.968	0.947	0.971	0.964	0.958	0.92	0.85(2)-0.86(2)	0.84(3)
Si-O-H	112.9(8)	113.6	116.7	113.6	116.66	115.6	114-120	120(2)-126(2)	117.7(7)-121.7(7)
C-Si-O-H	122.9(8)	123.4	120.8	123.8	124.7	124.2	-63--112	-144(2)-74(3)	-69(4)--96(4)
C-C-H	111.4(5)	111.5	110.3	111.4	111.8	109.6	109.5	109.9(1)-113.0(1)	109.5
C-C-C	108.4(3)	109.6	109.3	109.6	109.5	109.3	106.8(5)-111.7(4)	109.5(1), 109.8(2)	109.4(3)-110.7(3)
O-Si-O	107.7(3)	108.4	108.2	108.2	108.6	109.2	105.7(2)-110.5(2)	108.3(5), 111.0(8)	107.0(1)-109.6(1)

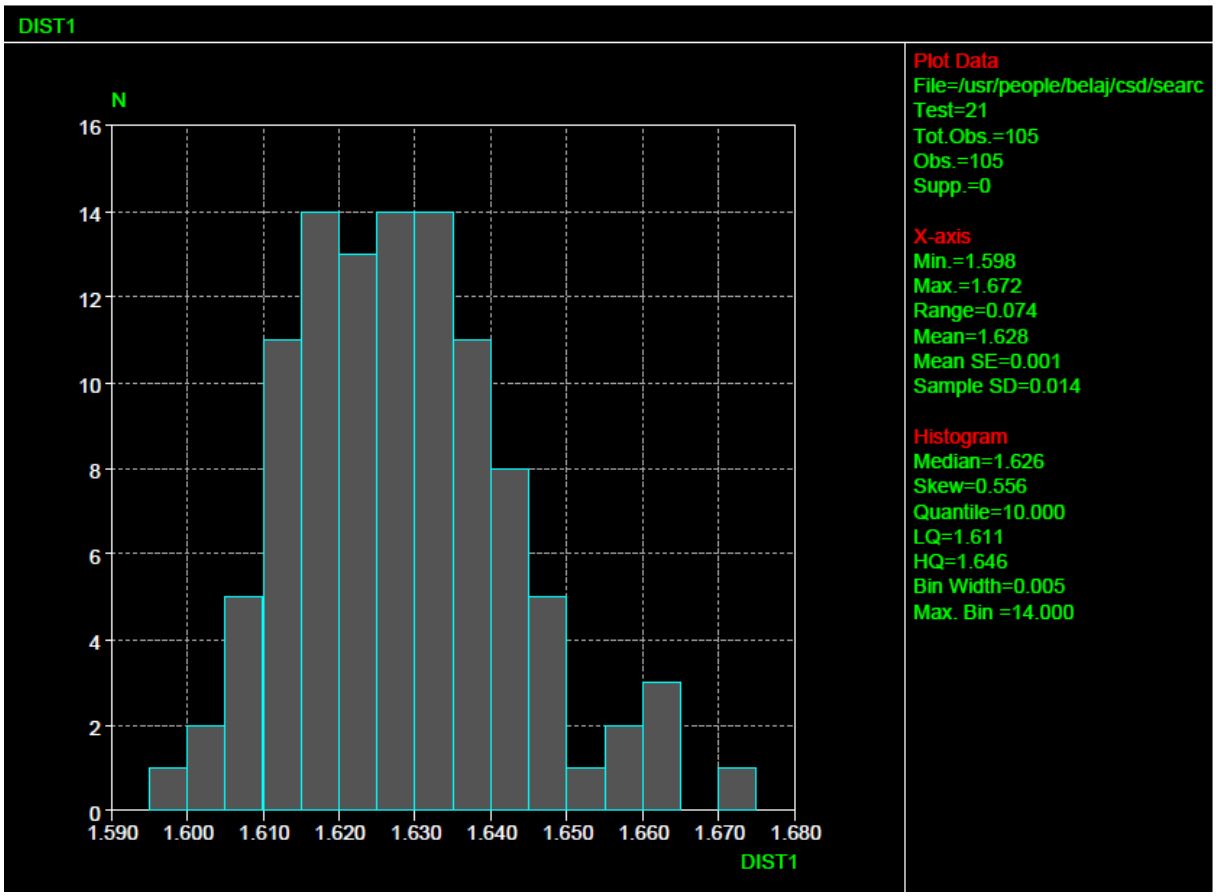


Fig.S2. VISTA-plot of the Si-O distances in the solid state for silanetriols obtained by X-ray crystallography.

Table S3. Independent parameters (p_n) and dependent parameters (d_n) used for the r_{h1} refinement of **1**.

Independent parameters

	Parameter	Value	Description
p_1	CSi	1.879(3)	Si-C distance
p_2	OSi	1.640(1)	Si-O distance
p_3	C1C2	1.540(2)	C-C distance
p_4	wCSiO	111.2(2)	C_q-Si-O-angle
p_5	wC2C1Si	110.5(3)	C_{Me}-C_q-Si-angle
p_6	C2H	1.118(3)	C-H distance
p_7	rOH	0.940(4)	O-H distance
p_8	wiC3	109.6(9)	Defines indirectly the C_q-C_{Me}-H_{Me} angle
p_9	wiSiO	112.9(8)	Si-O-H angle
p_{10}	wiSiO2	122.9(8)	C_q-Si-O-H dihedral

Dependent parameters

	Parameter	Value	
d_1	cch	111.4(5)	C_q-C_{Me}-H_{Me} angle
d_2	ccc	108.4(3)	C_{Me}-C_q-C_{Me}‘ – angle
d_3	osio	107.7(3)	O-Si-O‘ – angle

Table S5. Amplitudes of vibration for **1**.

Amplitudes of vibration

	Amplitude	d (r_a)	e.s.d.	u	e.s.d.	k	Area
u183	H(16)-O(19)	.9342	.0042	.0864	Tied to u178	.0019	12.5
u172	H(14)-O(17)	.9362	.0042	.0750	Tied to u178	.0019	12.5
u178	H(15)-O(18)	.9366	.0042	.0724	.0044	.0019	12.5
u42	C(3)-H(8)	1.1154	.0025	.0851	Tied to u46	.0038	7.9
u59	C(4)-H(9)	1.1154	.0025	.0851	Tied to u46	.0038	7.9
u22	C(2)-H(5)	1.1154	.0025	.0851	Tied to u46	.0038	7.9
u44	C(3)-H(10)	1.1155	.0025	.0844	Tied to u46	.0038	7.9
u24	C(2)-H(7)	1.1155	.0025	.0844	Tied to u46	.0038	7.9
u46	C(3)-H(12)	1.1155	.0025	.0844	.0031	.0038	7.9
u63	C(4)-H(13)	1.1155	.0025	.0844	Tied to u46	.0038	7.9
u61	C(4)-H(11)	1.1155	.0025	.0844	Tied to u46	.0038	7.9
u23	C(2)-H(6)	1.1155	.0025	.0844	Tied to u46	.0038	7.9
u1	C(1)-C(2)	1.5407	.0021	.0563	.0035	.0028	34.2
u2	C(1)-C(3)	1.5407	.0021	.0562	Tied to u1	.0028	34.2
u3	C(1)-C(4)	1.5407	.0021	.0562	Tied to u1	.0028	34.2
u190	O(19)-Si(20)	1.6413	.0009	.0389	Tied to u187	.0022	100.0
u189	O(18)-Si(20)	1.6413	.0009	.0389	Tied to u187	.0022	100.0
u187	O(17)-Si(20)	1.6413	.0009	.0385	.0014	.0022	100.0
u86	H(6)...H(7)	1.7973	.0091	.1300	Tied to u116	.0033	.8
u72	H(5)...H(7)	1.7973	.0091	.1306	Tied to u116	.0034	.8
u71	H(5)...H(6)	1.7973	.0091	.1306	Tied to u116	.0034	.8
u128	H(9)...H(13)	1.7973	.0091	.1305	Tied to u116	.0034	.8
u114	H(8)...H(10)	1.7973	.0091	.1305	Tied to u116	.0034	.8
u137	H(10)...H(12)	1.7974	.0091	.1300	Tied to u116	.0034	.8
u147	H(11)...H(13)	1.7974	.0091	.1300	Tied to u116	.0034	.8
u116	H(8)...H(12)	1.7974	.0091	.1305	.0105	.0035	.8
u126	H(9)...H(11)	1.7974	.0091	.1305	Tied to u116	.0035	.8
u19	C(1)-Si(20)	1.8788	.0026	.0507	.0031	.0009	65.5
u184	H(16)...Si(20)	2.1844	.0094	.1422	Tied to u175	.0091	9.4
u180	H(15)...Si(20)	2.1859	.0094	.1211	Tied to u175	.0080	9.4
u5	C(1)...H(6)	2.1991	.0065	.0872	Tied to u12	-.0058	4.0
u6	C(1)...H(7)	2.1991	.0065	.0871	Tied to u12	-.0058	4.0
u12	C(1)...H(13)	2.1992	.0065	.0869	.0041	-.0058	4.0
u11	C(1)...H(12)	2.1992	.0065	.0868	Tied to u12	-.0058	4.0
u10	C(1)...H(11)	2.1992	.0065	.0868	Tied to u12	-.0058	4.0
u9	C(1)...H(10)	2.1992	.0065	.0867	Tied to u12	-.0058	4.0
u7	C(1)...H(8)	2.1994	.0065	.0871	Tied to u12	-.0055	4.0
u8	C(1)...H(9)	2.1994	.0065	.0871	Tied to u12	-.0055	4.0
u4	C(1)...H(5)	2.1996	.0065	.0870	Tied to u12	-.0054	4.0
u175	H(14)...Si(20)	2.2932	.0094	.1536	.0099	.1194	8.9
u38	C(3)...C(4)	2.4952	.0051	.0927	Tied to u20	.0006	21.1
u20	C(2)...C(3)	2.4953	.0051	.0930	.0052	.0007	21.1
u21	C(2)...C(4)	2.4954	.0051	.0931	Tied to u20	.0008	21.1

*u*113	H(8)...H(9)	2.5169	.0254	.2891	Tied to *u*91	.0229	.6
*u*73	H(5)...H(8)	2.5177	.0254	.2869	Tied to *u*91	.0232	.6
*u*74	H(5)...H(9)	2.5178	.0254	.2866	Tied to *u*91	.0233	.6
*u*179	H(15)...O(19)	2.5483	.0153	.4753	Tied to *u*181	.0369	4.6
*u*138	H(10)...H(13)	2.5676	.0188	.2759	Tied to *u*91	.0236	.6
*u*103	H(7)...H(11)	2.5687	.0188	.2745	Tied to *u*91	.0244	.6
*u*91	H(6)...H(12)	2.5688	.0188	.2743	.0219	.0244	.6
*u*173	H(14)...O(18)	2.6029	.0158	.6617	Tied to *u*181	.1731	4.5
*u*181	H(16)...O(17)	2.6190	.0153	.4638	.0372	.1035	4.5
*u*186	O(17)...O(19)	2.6435	.0040	.0876	.0048	-.0016	35.5
*u*185	O(17)...O(18)	2.6436	.0040	.0875	Tied to *u*186	-.0015	35.5
*u*188	O(18)...O(19)	2.6462	.0040	.0853	Tied to *u*186	.0010	35.4
*u*58	C(4)...H(8)	2.7318	.0128	.2060	Tied to *u*29	-.0028	3.2
*u*43	C(3)...H(9)	2.7318	.0128	.2060	Tied to *u*29	-.0028	3.2
*u*39	C(3)...H(5)	2.7319	.0128	.2056	Tied to *u*29	-.0028	3.2
*u*55	C(4)...H(5)	2.7320	.0128	.2055	Tied to *u*29	-.0027	3.2
*u*25	C(2)...H(8)	2.7326	.0128	.2040	Tied to *u*29	-.0023	3.2
*u*26	C(2)...H(9)	2.7326	.0128	.2039	Tied to *u*29	-.0023	3.2
*u*47	C(3)...H(13)	2.7543	.0094	.2005	Tied to *u*29	-.0023	3.2
*u*60	C(4)...H(10)	2.7546	.0094	.1999	Tied to *u*29	-.0021	3.2
*u*28	C(2)...H(11)	2.7547	.0094	.2003	Tied to *u*29	-.0020	3.2
*u*29	C(2)...H(12)	2.7547	.0094	.1999	.0137	-.0020	3.2
*u*40	C(3)...H(6)	2.7551	.0094	.1984	Tied to *u*29	-.0018	3.2
*u*57	C(4)...H(7)	2.7552	.0094	.1984	Tied to *u*29	-.0017	3.2
*u*37	C(2)...Si(20)	2.8114	.0047	.0891	.0035	-.0021	43.8
*u*54	C(3)...Si(20)	2.8117	.0047	.0879	Tied to *u*37	-.0019	43.8
*u*70	C(4)...Si(20)	2.8117	.0047	.0879	Tied to *u*37	-.0019	43.8
*u*17	C(1)...O(18)	2.8973	.0048	.1441	Tied to *u*16	-.0028	24.3
*u*18	C(1)...O(19)	2.8974	.0048	.1438	Tied to *u*16	-.0027	24.3
*u*16	C(1)...O(17)	2.9011	.0048	.1177	.0075	-.0013	24.2
*u*139	H(10)...H(14)	2.9610	.0136	.6502	(fixed)	-.1985	.5
*u*94	H(6)...H(15)	2.9648	.0135	.6059	(fixed)	-.2116	.5
*u*111	H(7)...O(19)	2.9659	.0090	.4256	Tied to *u*153	.0538	4.0
*u*97	H(6)...O(18)	2.9668	.0090	.4254	Tied to *u*153	.0547	4.0
*u*166	H(13)...O(17)	2.9801	.0090	.3886	Tied to *u*153	.0579	3.9
*u*142	H(10)...O(17)	2.9813	.0090	.3856	Tied to *u*153	.0583	3.9
*u*160	H(12)...O(18)	2.9877	.0090	.3776	Tied to *u*153	.0627	3.9
*u*153	H(11)...O(19)	2.9898	.0090	.3752	.0297	.0641	3.9
*u*112	H(7)...Si(20)	3.0062	.0084	.2039	Tied to *u*99	-.0036	6.8
*u*99	H(6)...Si(20)	3.0063	.0084	.2036	.0149	-.0035	6.8
*u*162	H(12)...Si(20)	3.0068	.0084	.2015	Tied to *u*99	-.0033	6.8
*u*154	H(11)...Si(20)	3.0068	.0084	.2013	Tied to *u*99	-.0033	6.8
*u*169	H(13)...Si(20)	3.0072	.0084	.2003	Tied to *u*99	-.0031	6.8
*u*145	H(10)...Si(20)	3.0073	.0084	.2004	Tied to *u*99	-.0030	6.8
*u*150	H(11)...H(16)	3.0352	.0134	.5390	(fixed)	-.1645	.5
*u*117	H(8)...H(13)	3.0761	.0134	.3060	(fixed)	-.0173	.5
*u*125	H(9)...H(10)	3.0763	.0134	.3058	(fixed)	-.0172	.5

*u*77	H(5)...H(12)	3.0763	.0134	.3065	(fixed)	-.0170	.5
*u*76	H(5)...H(11)	3.0764	.0134	.3063	(fixed)	-.0170	.5
*u*101	H(7)...H(9)	3.0778	.0134	.3028	(fixed)	-.0163	.5
*u*87	H(6)...H(8)	3.0778	.0134	.3026	(fixed)	-.0163	.5
*u*171	H(14)...H(16)	3.1570	.0243	1.0880	(fixed)	.3255	.5
*u*170	H(14)...H(15)	3.1608	.0243	1.0822	(fixed)	.3253	.5
*u*182	H(16)...O(18)	3.2241	.0114	.4795	Tied to *u*174	.0385	3.6
*u*177	H(15)...O(17)	3.2937	.0113	.4589	Tied to *u*174	.1022	3.6
*u*174	H(14)...O(19)	3.2984	.0116	.6574	.0535	.1749	3.6
*u*36	C(2)...O(19)	3.3413	.0044	.2888	Tied to *u*67	.0063	21.1
*u*35	C(2)...O(18)	3.3415	.0044	.2890	Tied to *u*67	.0066	21.1
*u*67	C(4)...O(17)	3.3467	.0044	.2647	.0083	.0078	21.0
*u*51	C(3)...O(17)	3.3475	.0044	.2626	Tied to *u*67	.0083	21.0
*u*52	C(3)...O(18)	3.3512	.0044	.2571	Tied to *u*67	.0111	21.0
*u*69	C(4)...O(19)	3.3522	.0044	.2556	Tied to *u*67	.0119	21.0
*u*14	C(1)...H(15)	3.3684	.0097	.2448	Tied to *u*27	-.1758	2.6
*u*15	C(1)...H(16)	3.3746	.0096	.1838	Tied to *u*27	-.1769	2.6
*u*176	H(15)...H(16)	3.3785	.0228	.6911	(fixed)	.3264	.4
*u*13	C(1)...H(14)	3.4098	.0096	.1777	Tied to *u*27	-.1424	2.6
*u*32	C(2)...H(15)	3.4635	.0117	.4548	.0364	-.2325	2.5
*u*62	C(4)...H(12)	3.4659	.0063	.1265	Tied to *u*27	-.0201	2.5
*u*45	C(3)...H(11)	3.4659	.0063	.1265	Tied to *u*27	-.0201	2.5
*u*30	C(2)...H(13)	3.4660	.0063	.1269	Tied to *u*27	-.0200	2.5
*u*27	C(2)...H(10)	3.4660	.0063	.1266	.0077	-.0200	2.5
*u*56	C(4)...H(6)	3.4661	.0063	.1266	Tied to *u*27	-.0199	2.5
*u*41	C(3)...H(7)	3.4661	.0063	.1265	Tied to *u*27	-.0199	2.5
*u*48	C(3)...H(14)	3.4739	.0117	.5013	Tied to *u*32	-.2103	2.5
*u*163	H(13)...H(14)	3.5025	.0112	.6620	(fixed)	-.1977	.4
*u*156	H(12)...H(14)	3.5034	.0127	.7709	(fixed)	-.1901	.4
*u*66	C(4)...H(16)	3.5108	.0116	.4119	Tied to *u*32	-.1951	2.5
*u*108	H(7)...H(16)	3.5166	.0112	.5674	(fixed)	-.2141	.4
*u*107	H(7)...H(15)	3.5166	.0125	.6219	(fixed)	-.2309	.4
*u*157	H(12)...H(15)	3.5653	.0112	.5767	(fixed)	-.1626	.4
*u*165	H(13)...H(16)	3.5757	.0125	.6317	(fixed)	-.1686	.4
*u*151	H(11)...O(17)	3.6190	.0052	.4284	.0327	-.0210	3.2
*u*110	H(7)...O(18)	3.6205	.0052	.4189	Tied to *u*151	-.0217	3.2
*u*159	H(12)...O(17)	3.6205	.0052	.4260	Tied to *u*151	-.0200	3.2
*u*98	H(6)...O(19)	3.6207	.0052	.4159	Tied to *u*151	-.0221	3.2
*u*143	H(10)...O(18)	3.6281	.0052	.4081	Tied to *u*151	-.0165	3.2
*u*168	H(13)...O(19)	3.6288	.0052	.4080	Tied to *u*151	-.0158	3.2
*u*115	H(8)...H(11)	3.7436	.0148	.1998	(fixed)	-.0291	.4
*u*127	H(9)...H(12)	3.7436	.0148	.1997	(fixed)	-.0291	.4
*u*75	H(5)...H(10)	3.7437	.0148	.1990	(fixed)	-.0291	.4
*u*78	H(5)...H(13)	3.7437	.0148	.1990	(fixed)	-.0291	.4
*u*100	H(7)...H(8)	3.7443	.0148	.1983	(fixed)	-.0285	.4
*u*88	H(6)...H(9)	3.7444	.0148	.1981	(fixed)	-.0285	.4
*u*155	H(12)...H(13)	3.7721	.0110	.1939	(fixed)	-.0281	.4

*u*136	H(10)...H(11)	3.7721	.0110	.1935	(fixed)	-.0281	.4
*u*90	H(6)...H(11)	3.7724	.0110	.1931	(fixed)	-.0279	.4
*u*104	H(7)...H(12)	3.7724	.0110	.1928	(fixed)	-.0279	.4
*u*89	H(6)...H(10)	3.7726	.0110	.1926	(fixed)	-.0277	.4
*u*105	H(7)...H(13)	3.7726	.0110	.1925	(fixed)	-.0277	.4
*u*85	H(5)...Si(20)	3.7963	.0049	.1177	Tied to *u*124	-.0262	5.4
*u*135	H(9)...Si(20)	3.7964	.0049	.1173	Tied to *u*124	-.0261	5.4
*u*124	H(8)...Si(20)	3.7964	.0049	.1172	.0078	-.0261	5.4
*u*33	C(2)...H(16)	3.9344	.0072	.4055	Tied to *u*49	-.2342	2.2
*u*64	C(4)...H(14)	3.9387	.0072	.5005	Tied to *u*49	-.2095	2.2
*u*49	C(3)...H(15)	3.9690	.0072	.4393	.0356	-.1929	2.2
*u*68	C(4)...O(18)	4.1899	.0026	.1041	Tied to *u*34	-.0387	16.8
*u*53	C(3)...O(19)	4.1903	.0026	.1035	Tied to *u*34	-.0383	16.8
*u*34	C(2)...O(17)	4.1910	.0026	.0904	.0032	-.0382	16.8
*u*148	H(11)...H(14)	4.2823	.0064	.7749	(fixed)	-.1887	.3
*u*95	H(6)...H(16)	4.2915	.0063	.5998	(fixed)	-.2318	.3
*u*146	H(11)...H(12)	4.3336	.0114	.1424	(fixed)	-.0387	.3
*u*92	H(6)...H(13)	4.3338	.0114	.1428	(fixed)	-.0385	.3
*u*102	H(7)...H(10)	4.3340	.0114	.1428	(fixed)	-.0383	.3
*u*140	H(10)...H(15)	4.3464	.0063	.6393	(fixed)	-.1662	.3
*u*84	H(5)...O(19)	4.3555	.0049	.2711	Tied to *u*83	-.0206	2.7
*u*83	H(5)...O(18)	4.3557	.0049	.2709	.0204	-.0204	2.7
*u*132	H(9)...O(17)	4.3576	.0049	.2425	Tied to *u*83	-.0218	2.7
*u*121	H(8)...O(17)	4.3583	.0049	.2414	Tied to *u*83	-.0213	2.7
*u*122	H(8)...O(18)	4.3612	.0049	.2424	Tied to *u*83	-.0183	2.7
*u*134	H(9)...O(19)	4.3618	.0049	.2413	Tied to *u*83	-.0178	2.7
*u*152	H(11)...O(18)	4.4548	.0082	.2254	(fixed)	-.0538	2.6
*u*161	H(12)...O(19)	4.4552	.0082	.2245	(fixed)	-.0535	2.6
*u*167	H(13)...O(18)	4.4561	.0082	.2245	(fixed)	-.0526	2.6
*u*96	H(6)...O(17)	4.4563	.0082	.2323	(fixed)	-.0516	2.6
*u*109	H(7)...O(17)	4.4564	.0082	.2304	(fixed)	-.0517	2.6
*u*144	H(10)...O(19)	4.4570	.0082	.2244	(fixed)	-.0517	2.6
*u*118	H(8)...H(14)	4.4987	.0120	.4593	(fixed)	-.2881	.3
*u*80	H(5)...H(15)	4.4993	.0120	.4514	(fixed)	-.2890	.3
*u*131	H(9)...H(16)	4.5371	.0120	.3947	(fixed)	-.2611	.3
*u*65	C(4)...H(15)	4.6318	.0101	.2230	.0158	-.1787	1.9
*u*50	C(3)...H(16)	4.6339	.0101	.1899	Tied to *u*65	-.1794	1.9
*u*31	C(2)...H(14)	4.6755	.0101	.1795	Tied to *u*65	-.1386	1.9
*u*149	H(11)...H(15)	4.7370	.0125	.3149	(fixed)	-.1676	.3
*u*141	H(10)...H(16)	4.7573	.0125	.3321	(fixed)	-.1450	.3
*u*93	H(6)...H(14)	4.7937	.0125	.3570	(fixed)	-.1051	.3
*u*129	H(9)...H(14)	4.8677	.0080	.4663	(fixed)	-.2875	.3
*u*81	H(5)...H(16)	4.8756	.0080	.3971	(fixed)	-.2911	.3
*u*119	H(8)...H(15)	4.9011	.0080	.4422	(fixed)	-.2583	.3
*u*158	H(12)...H(16)	4.9992	.0100	.3021	(fixed)	-.1674	.3
*u*164	H(13)...H(15)	5.0178	.0100	.3354	(fixed)	-.1447	.3
*u*82	H(5)...O(17)	5.0335	.0064	.1294	Tied to *u*133	-.0611	2.3

*u*133	H(9)...O(18)	5.0361	.0064	.1434	.0118	-.0578	2.3
*u*123	H(8)...O(19)	5.0362	.0064	.1430	Tied to *u*133	-.0577	2.3
*u*106	H(7)...H(14)	5.0557	.0100	.3532	(fixed)	-.1044	.3
*u*130	H(9)...H(15)	5.4537	.0099	.2510	(fixed)	-.2456	.3
*u*120	H(8)...H(16)	5.4557	.0099	.2056	(fixed)	-.2473	.3
*u*79	H(5)...H(14)	5.4728	.0099	.2019	(fixed)	-.2304	.3

Table S6. Least squares correlation matrix. All elements are scaled by a factor of 100, and only off-diagonal elements with absolute values >50% are included.

	*p*3	*p*4	*p*5	*p*8	*u*13	*u*26	*u*52	*u*151	*u*173	*u*185	*k*2
*p*2	-56										
*p*3	100	-53									
*p*4		100	-53		-55	53					
*p*5			100	79	60						
*p*7							60				
*p*8				100	55						
*u*3										69	
*u*13					100						
*u*26						100			58		
*u*50									68		
*u*52							100	57			
*u*185										100	60
*k*2											100

Table S7. Restraints used for the refinement of **1**.

Non-ed Data

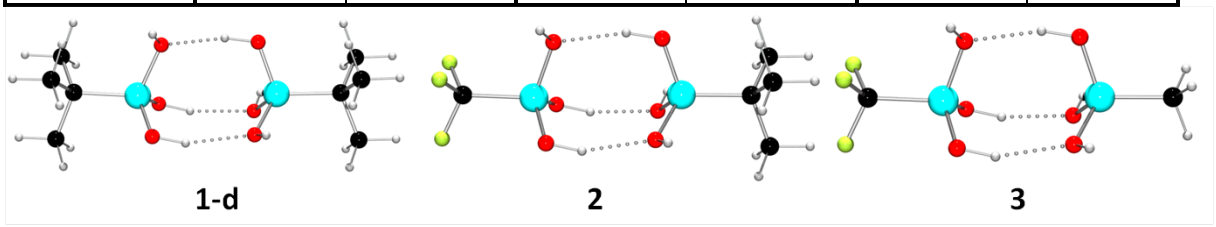
Name	Type	Value	Refined	Difference	Uncertainty
wiSiO	Parameter	113.0000	112.8749	.1251	1.0000
wiSiO2	Parameter	123.0000	122.9103	.0897	1.0000
*u*1	Amplitude	.0541	.0563	-.0022	.0054
*u*12	Amplitude	.1119	.0869	.0250	.0080
*u*16	Amplitude	.1126	.1177	-.0051	.0120
*u*20	Amplitude	.0830	.0930	-.0100	.0080
*u*27	Amplitude	.1089	.1266	-.0177	.0110
*u*29	Amplitude	.1857	.1999	-.0142	.0180
*u*32	Amplitude	.4524	.4548	-.0024	.0450
*u*34	Amplitude	.1037	.0904	.0133	.0100
*u*49	Amplitude	.4442	.4393	.0049	.0440
*u*65	Amplitude	.2025	.2230	-.0205	.0200
*u*67	Amplitude	.2766	.2647	.0119	.0270
*u*83	Amplitude	.3101	.2709	.0392	.0310
*u*91	Amplitude	.2714	.2743	-.0029	.0270
*u*99	Amplitude	.2156	.2036	.0120	.0220
*u*116	Amplitude	.1274	.1305	-.0031	.0130
*u*124	Amplitude	.1178	.1172	.0006	.0110
*u*133	Amplitude	.1654	.1434	.0220	.0160
*u*151	Amplitude	.4170	.4284	-.0114	.0420
*u*153	Amplitude	.3836	.3752	.0084	.0380
*u*174	Amplitude	.6585	.6574	.0011	.0660
*u*175	Amplitude	.1743	.1536	.0207	.0130
*u*178	Amplitude	.0741	.0724	.0017	.0080
*u*181	Amplitude	.4620	.4638	-.0018	.0460
*u*186	Amplitude	.0916	.0876	.0040	.0100

Table S8. Amplitude constraints used for the refinement of **1**.

*u*1	= 1.0019**u*2	*u30*	= .8729**u*53	*u*99	= 1.0165**u*169
*u*1	= 1.0019**u*3	*u*34	= .8685**u*68	*u*116	=1.0000**u*128
*u*12	= 1.0009**u*11	*u*37	= 1.0140**u*54	*u*116	= .9992**u*72
*u*12	= .9964**u*5	*u*37	= 1.0140**u*70	*u*116	= .9992**u*71
*u*12	= 1.0018**u*9	*u*46	= 1.0000**u*44	*u*116	= 1.0039**u*86
*u*12	= 1.0009**u*10	*u*46	= 1.0000**u*24	*u*116	= 1.0000**u*114
*u*12	= .9973**u*7	*u*46	= 1.0000**u*23	*u*116	= 1.0039**u*147
*u*12	= .9973**u*6	*u*46	= .9923**u*42	*u*116	= 1.0000**u*126
*u*12	= .9973**u*8	*u*46	= .9923**u*59	*u*116	= 1.0039**u*137
*u*12	= .9982**u*4	*u*46	= .9923**u*22	*u*124	= .9992**u*135
*u*16	= .8171**u*17	*u*46	= 1.0000**u*61	*u*124	= .9958**u*85
*u*16	= .8189**u*18	*u*46	= 1.0000**u*63	*u*133	= 1.0030**u*123
*u*20	= 1.0036**u*38	*u*49	= .8777**u*64	*u*133	= 1.1078**u*82
*u*20	= .9988**u*21	*u*49	= 1.0832**u*33	*u*151	= 1.0496**u*143
*u*27	= 1.0009**u*41	*u*65	= 1.1739**u*50	*u*151	= 1.0498**u*168
*u*27	= 1.0000**u*56	*u*65	= 1.2423**u*31	*u*151	= 1.0226**u*110
*u*27	= 1.0009**u*45	*u*67	= 1.0298**u*52	*u*151	= 1.0299**u*98
*u*27	= 1.0009**u*62	*u*67	=.9159**u*35	*u*151	= 1.0055**u*159
*u*27	= .9982**u*30	*u*67	= 1.0356**u*69	*u*153	= .8820**u*97
*u*27	= .5173**u*14	*u*67	= 1.0080**u*51	*u*153	= .9935**u*160
*u*27	= .7127**u*13	*u*67	= .9168**u*36	*u*153	= .9655**u*166
*u*27	= .6888**u*15	*u*83	= 1.1227**u*134	*u*153	= .9729**u*142
*u*29	= 1.0076**u*40	*u*83	= 1.1179**u*122	*u*153	= .8816**u*111
*u*29	= .9973**u*47	*u*83	= 1.1171**u*132	*u*174	= 1.4325**u*177
*u*29	= 1.0076**u*57	*u*83	= .9994**u*84	*u*174	= 1.3710**u*182
*u*29	= 1.0000**u*60	*u*83	= 1.1223**u*121	*u*175	= 1.0806**u*184
*u*29	= .9984**u*28	*u*91	= .9941**u*138	*u*175	= 1.2686**u*180
*u*29	= .9723**u*39	*u*91	= .9993**u*103	*u*178	= .9648**u*172
*u*29	= .9799**u*25	*u*91	= .9560**u*73	*u*178	= .8382**u*183
*u*29	= .9707**u*58	*u*91	= .9490**u*113	*u*181	= .7010**u*173
*u*29	= .9728**u*55	*u*91	= .9570**u*74	*u*181	= .9759**u*179
*u*29	= .9707**u*43	*u*99	= 1.0160**u*145	*u*186	= 1.0269**u*188
*u*29	= .9805**u*26	*u*99	= 1.0113**u*154	*u*186	= 1.0011**u*185
*u*32	= 1.1040**u*66	*u*99	= 1.0103**u*162	*u*187	= .9896**u*189
*u*32	= .9072**u*48	*u*99	= .9986**u*112	*u*187	= .9896**u*190

Table S9. Comparison of geometric parameters of hydrogen-bonded dimers **1-d**, **2** and **3** calculated at the B3LYP/6-31++g** level of theory.

	1-d		**2**		**3**	
	^{t}BuSi(OH)$_3$·^{t}BuSi(OH)$_3$		**CF$_3$Si(OH)$_3$· ^{t}BuSi(OH)$_3$**		**CF$_3$Si(OH)$_3$· MeSi(OH)$_3$**	
Si-O1	1.704	1.645	1.667	1.647	1.677	1.644
Si-O2	1.647	1.681	1.629	1.683	1.629	1.637
Si-O3	1.658	1.682	1.638	1.683	1.638	1.681
Si-O1-H1	114.7	116.4	116.0	117.4	116.1	117.4
Si-O2-H2	117.8	115.5	117.5	115.5	117.6	115.9
Si-O3-H3	115.2	115.8	115.1	115.8	115.2	116.2
O1-H1···O1'	-	166.5	-	163.3	-	163.0
O2-H2···O2'	164.1	-	161.1	-	160.9	-
O3-H3···O3'	161.2	-	158.0	-	157.9	-
O1···O1‘	2.825	2.825	2.910	2.910	2.903	2.903
O2···O2‘	2.889	2.889	2.846	2.846	2.849	2.849
O3···O3‘	2.942	2.942	2.894	2.894	2.897	2.897



1-d **2** **3**

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