Supplementary Materials: σ-Bond Electron Delocalization in Oligosilanes as Function of Substitution Pattern, Chain Length, and Spatial Orientation

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Table S1. Crystallographic data for compounds **9**, **14**, **15**, and **16a**.

	9	**14**	**15**	**16a**
Empirical formula	$Si_{10}C_{34}H_{90}$	$Si_{18}C_{38}H_{114}$	$Si_{10}C_{34}H_{82}$	$Si_4C_{21}H_{51}KO_9$
M_w	779.96	1076.91	771.90	599.08
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Size [mm]	0.44 × 0.34 × 0.18	0.32 × 0.22 × 0.20	0.40 × 0.24 × 0.10	0.22 × 0.15 × 0.12
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	C2/c	P-1	P-1	Pbca
a [Å]	19.449(4)	9.941(2)	9.603(2)	17.927(6)
b [Å]	9.1445(2)	14.054(3)	15.262(3)	18.514(7)
c [Å]	28.606(6)	15.042(3)	18.530(4)	19.920(7)
α [°]	90	117.16(3)	106.80(3)	90
β [°]	103.34(3)	96.81(3)	102.56(3)	90
γ [°]	90	103.20(3)	106.32(3)	90
V [Å^3]	4950.0(2)	1759(2)	2360(2)	6612(4)
Z	4	1	2	8
ρ_{calc} [gcm^{-3}]	1.046	1.017	1.086	1.204
Absorption coefficient [mm^{-1}]	0.287	0.346	0.300	0.346
F(000)	1736	594	852	2592
θ range	1.46 < θ < 26.37	1.57 < θ < 23.50	1.21 < θ < 26.37	1.88 < θ < 25.25
Reflections collected/unique	19231/5066	11205/5173	16509/8754	43966/5979
Completeness to θ [%]	99.9	99.5	96.8	100
Data/restraints/parameters	5066/0/213	5173/0/272	8754/0/417	5979/0/325
Goodness of fit on F^2	1.07	1.04	1.14	1.26
Final R indices [I > 2σ(I)]	R1 = 0.034, *w*R2 = 0.083	R1 = 0.099, *w*R2 = 0.247	R1 = 0.080, *w*R2 = 0.221	R1 = 0.093, *w*R2 = 0.206
R indices (all data)	R1 = 0.042, *w*R2 = 0.087	R1 = 0.168, *w*R2 = 0.294	R1 = 0.111, *w*R2 = 0.258	R1 = 0.108, *w*R2 = 0.214
Largest diff. Peak/hole [e$^-$/Å^3]	0.50/−0.18	1.44/−0.47	1.54/−1.35	1.25/−0.47

Table S2. Crystallographic data for compounds **17**, **18**, **18a**, and **23**.

	17	**18**	**18a**	**23**
Empirical formula	$Si_{10}C_{48}H_{86}$	$Si_{10}C_{32}H_{70}$	$Si_8C_{50}H_{100}K_2O_{12}$	$Si_5C_{25}H_{46}$
M_w	944.07	735.78	1196.22	487.07
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Size [mm]	0.26 × 0.18 × 0.14	0.38 × 0.22 × 0.12	0.48 × 0.36 × 0.28	0.28 × 0.24 × 0.12
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	P2(1)/n	Cc	P2(1)/c
a [Å]	13.115(3)	12.147(2)	15.024(3)	10.594(2)
b [Å]	15.143(3)	9.463(2)	20.707(4)	18.139(4)
c [Å]	16.005(3)	22.116(4)	22.101(4)	15.919(3)
α [°]	102.673(3)	90	90	90
β [°]	91.018(3)	100.22(3)	92.50(3)	95.11(3)
γ [°]	113.981(3)	90	90	90
V [Å^3]	2813(2)	2502(2)	6869(3)	3047(2)
Z	2	2	4	4
ρ_{calc} [gcm^{-3}]	1.115	0.977	1.157	1.062
Absorption coefficient [mm^{-1}]	0.263	0.281	0.327	0.245
F(000)	1028	804	2584	1064
θ range	1.52 < θ < 26.37	1.79 < θ < 26.35	1.68 < θ < 26.37	1.71 < θ < 26.37
Reflections collected/unique	22690/11347	15247/4995	19475/10423	24118/6202
Completeness to θ [%]	98.5	97.8	94.8	99.5
Data/restraints/parameters	11347/0/545	4995/0/200	10423/2/663	6202/0/283
Goodness of fit on F^2	1.07	1.27	1.15	0.98
Final R indices [I > 2σ(I)]	R1 = 0.050, *w*R2 = 0.119	R1 = 0.064, *w*R2 = 0.132	R1 = 0.065, *w*R2 = 0.159	R1 = 0.048, *w*R2 = 0.108
R indices (all data)	R1 = 0.058, *w*R2 = 0.123	R1 = 0.072, *w*R2 = 0.137	R1 = 0.067, *w*R2 = 0.159	R1 = 0.073, *w*R2 = 0.116
Largest diff. Peak/hole [e$^-$/Å^3]	0.74/−0.31	0.62/−0.33	2.44/−0.42	0.42/−0.25

Table S3. Crystallographic data for compounds **21a**, **21b**, **22**, and **24**.

	21a	**21b**	**22**	**24**
Empirical formula	$Si_{10}C_{32}H_{84}$	$Si_{10}C_{32}H_{84}$	$Si_9C_{28}H_{58}$	$Si_5C_{24}H_{56}$
M_w	749.89	749.89	647.55	485.14
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Size [mm]	0.34 × 0.26 × 0.12	0.30 × 0.30 × 0.26	0.38 × 0.27 × 0.18	0.42 × 0.25 × 0.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	P2(1)/n	P2(1)/c
a [Å]	16.054(2)	36.810(7)	13.371(3)	19.296(4)
b [Å]	10.615(2)	9.195(2)	20.559(4)	9.368(2)
c [Å]	27.564(5)	31.596(6)	14.604(3)	18.715(4)
$\alpha = \gamma = 90°$; β [°]	99.26(3)	117.88(3)	91.24(3)	114.64(3)
V [Å^3]	4636(2)	9453(3)	4014(2)	3075(2)
Z	4	8	4	4
ρ_{calc} [gcm^{-3}]	1.074	1.054	1.072	1.048
Absorption coefficient [mm^{-1}]	0.304	0.298	0.314	0.242
F(000)	1664	3328	1408	1080
θ range	$1.50 < \theta < 25.00$	$1.25 < \theta < 26.37$	$1.71 < \theta < 26.38$	$2.18 < \theta < 26.35$
Reflections collected/unique	13825/4066	36797/9665	28438/8149	23776/6262
Completeness to θ [%]	99.3	99.8	99.1	99.8
Data/restraints/parameters	4066/0/203	9665/0/405	8149/0/350	6262/0/282
Goodness of fit on F^2	1.30	1.09	1.03	1.04
Final R indices [$I > 2\sigma(I)$]	R1 = 0.095, *w*R2 = 0.184	R1 = 0.035, *w*R2 = 0.083	R1 = 0.046, *w*R2 = 0.123	R1 = 0.070, *w*R2 = 0.173
R indices (all data)	R1 = 0.112, *w*R2 = 0.190	R1 = 0.040, *w*R2 = 0.085	R1 = 0.056, *w*R2 = 0.127	R1 = 0.073, *w*R2 = 0.176
Largest diff. Peak/hole [e$^-$/Å^3]	0.82/−0.49	0.47/−0.21	0.57/−0.35	2.23/−1.40