Table S1 Molecular geometries of the C_2 structure of 1,1,2,2-tetra-*tert*-butyldisilane and the C_1 structure of 1,1,1,2-tetra-*tert*-butyldisilane at the HF level of theory with the 3-21G* and 6-31G* basis sets.[a,b]

1,1,2,2-tetra-*tert*-butyldisilane			1,1,1,2-tetra-*tert*-butyldisilane		
Parameter	HF/3-21G*	HF/6-31G*	Parameter	HF/3-21G*	HF/6-31G*
Si(1)-Si(2)	241.3	243.5	Si(1)-Si(2)	239.8	244.2
Si(2)-C(3)	192.6	194.6	Si(1)-C(19)	195.1	197.6
Si(2)-C(16)	193.1	195.1	Si(1)-C(32)	195.4	198.0
Si(2)-H(29)	148.6	148.5	Si(1)-C(45)	194.5	197.1
C-C (mean)	155.3	154.2	Si(2)-C(6)	192.4	193.8
C-H (mean)	108.5	108.6	Si(2)-H(3)	148.6	148.5
Si(1)-Si(2)-C(3)	108.1	108.6	Si(2)-H(4)	148.6	148.5
Si(1)-Si(2)-C(16)	120.7	120.4	C-C (mean)	155.4	154.3
C(3)-Si(2)-C(16)	115.6	115.6	C-H (mean)	108.4	108.5
Si(2)-C(3)-C(4)	112.8	112.6	Si(2)-Si(1)-C(19)	107.9	108.1
Si(2)-C(3)-C(5)	112.6	111.7	Si(2)-Si(1)-C(32)	102.9	102.9
Si(2)-C(3)-C(6)	108.0	108.2	Si(2)-Si(1)-C(45)	110.4	110.8
Si(2)-C(16)-C(17)	110.1	109.8	Si(1)-Si(2)-C(6)	129.2	129.4
Si(2)-C(16)-C(18)	109.2	108.6	Si(1)-Si(2)-H(3)	106.2	105.7
Si(2)-C(16)-C(19)	114.8	114.6	Si(1)-Si(2)-H(4)	105.4	105.0
C(4)-C(3)-Si(2)-Si(1)	57.9	60.0	C(19)-Si(1)-C(32)	111.2	111.1
C(17)-C(16)-Si(2)-Si(1)	34.5	32.0	C(19)-Si(1)-C(45)	112.3	112.0
H(30)-Si(1)-Si(2)-H(29)	-98.7	-101.4	C(32)-Si(1)-C(45)	111.7	111.5
			C(32)-Si(1)-Si(2)-C(6)	-161.8	-162.6
Energy[c]	-1199.5665	-1205.8378	Energy[c]	-1199.5566	-1205.8255

[a] All bond lengths in pm, all angles in °.

[b] See Figure 2 in main text for atom numbering.

[c] Absolute energy in Hartrees.

Table S2 Interatomic distances (r/pm) and amplitudes of vibration (u/pm) for the GED structure of 1,1,2,2-tetra-*tert*-butyldisilane.[a,b,c]

No.	Atom Pair	r_a / pm	u /pm[b]	Restraint	No.	Atom Pair	r_a / pm	u /pm[b]	Restraint
u_1	Si(1)-Si(2)	245.3(8)	6.3(6)	6.7(7)	u_{70}	C(19)...C(34)	392.2(39)	12.2(*tied to* u_{59})	
u_2	Si(1)-C(31)	194.4(2)	4.9(2)		u_{71}	C(3)...C(31)	435.3(36)	15.7(*tied to* u_{59})	
u_3	Si(2)-C(3)	194.4(2)	4.9(*tied to* u_2)		u_{72}	C(3)...C(34)	446.4(43)	12.3(*tied to* u_{59})	
u_4	Si(2)-C(16)	194.4(2)	5.0(*tied to* u_2)		u_{73}	C(6)...C(31)	446.4(43)	12.3(*tied to* u_{59})	
u_5	Si(1)-C(44)	194.4(2)	5.0(*tied to* u_2)		u_{74}	C(6)...C(32)	386.3(62)	26.2(32)	26.8(27)
u_6	Si(2)...C(17)	281.9(15)	7.8(7)	9.4(9)	u_{75}	C(4)...C(34)	386.3(62)	26.2(*tied to* u_{74})	
u_7	Si(1)...C(34)	279.8(19)	7.5(*tied to* u_6)		u_{76}	C(3)...C(44)	323.6(15)	8.9(*tied to* u_{74})	
u_8	Si(2)...C(6)	279.8(19)	7.5(*tied to* u_6)		u_{77}	C(3)...C(16)	323.6(15)	8.9(*tied to* u_{74})	
u_9	Si(1)...C(45)	281.9(15)	7.8(*tied to* u_6)		u_{78}	C(3)...C(32)	411.2(34)	24.1(*tied to* u_{74})	
u_{10}	Si(2)...C(19)	286.4(15)	7.4(*tied to* u_6)		u_{79}	C(4)...C(31)	411.2(34)	24.1(*tied to* u_{74})	
u_{11}	Si(1)...C(47)	286.4(15)	7.4(*tied to* u_6)		u_{80}	C(5)...C(18)	357.6(44)	17.7(21)	17.3(17)
u_{12}	Si(1)...C(33)	287.5(16)	7.4(*tied to* u_6)		u_{81}	C(33)...C(46)	357.6(44)	17.7(*tied to* u_{80})	
u_{13}	Si(2)...C(5)	287.5(16)	7.4(*tied to* u_6)		u_{82}	C(6)...C(44)	435.1(41)	16.1(*tied to* u_{80})	
u_{14}	Si(2)...C(4)	296.2(13)	7.3(*tied to* u_6)		u_{83}	C(16)...C(34)	435.1(41)	16.1(*tied to* u_{80})	
u_{15}	Si(1)...C(32)	296.2(13)	7.3(*tied to* u_6)		u_{84}	C(6)...C(45)	442.7(94)	26.0(*tied to* u_{80})	
u_{16}	Si(2)...C(18)	299.7(10)	7.2(*tied to* u_6)		u_{85}	C(17)...C(34)	442.7(94)	26.0(*tied to* u_{80})	
u_{17}	Si(1)...C(46)	299.7(10)	7.2(*tied to* u_6)		u_{86}	C(31)...C(46)	391.4(29)	14.0(*tied to* u_{80})	
u_{18}	Si(2)...C(31)	375.6(12)	10.3(14)	10.6(11)	u_{87}	C(3)...C(18)	391.4(29)	14.0(*tied to* u_{80})	
u_{19}	Si(1)...C(17)	351.1(23)	16.2(*tied to* u_{18})		u_{88}	C(3)...C(17)	451.9(14)	10.1(*tied to* u_{80})	
u_{20}	Si(2)...C(45)	351.1(23)	16.2(*tied to* u_{18})		u_{89}	C(31)...C(45)	451.9(14)	10.1(*tied to* u_{80})	
u_{21}	Si(1)...C(3)	375.6(12)	10.3(*tied to* u_{18})		u_{90}	C(6)...C(34)	502.5(64)	17.9(*tied to* u_{80})	
u_{22}	Si(2)...C(34)	392.9(13)	10.3(*tied to* u_{18})		u_{91}	Si(1)-H(30)	151.6(12)	8.2(11)	8.7(8)
u_{23}	Si(1)...C(6)	392.9(13)	10.3(*tied to* u_{18})		u_{92}	Si(2)-H(29)	151.6(12)	8.2(*tied to* u_{91})	
u_{24}	Si(1)...C(16)	362.3(15)	11.3(12)	10.2(11)	u_{93}	C(4)...C(33)	564.1(34)	22.7(20)	28.8(30)
u_{25}	Si(2)...C(44)	362.3(15)	11.3(*tied to* u_{25})		u_{94}	C(6)...C(16)	453.1(19)	10.5(*tied to* u_{93})	
u_{26}	Si(1)...C(4)	420.2(17)	17.1(*tied to* u_{25})		u_{95}	C(34)...C(44)	453.1(19)	10.5(*tied to* u_{93})	
u_{27}	Si(2)...C(32)	420.2(17)	17.1(*tied to* u_{25})		u_{96}	C(4)...C(18)	468.2(39)	13.2(*tied to* u_{93})	
u_{28}	C(3)-C(6)	155.7(1)	4.2(2)		u_{97}	C(32)...C(46)	468.2(39)	13.2(*tied to* u_{93})	
u_{29}	C(31)-C(34)	155.7(1)	4.2(*tied to* u_{28})		u_{98}	C(17)...C(45)	472.7(100)	24.9(*tied to* u_{93})	
u_{30}	C(16)-C(17)	155.7(1)	4.2(*tied to* u_{28})		u_{99}	C(16)...C(31)	477.0(27)	12.1(*tied to* u_{93})	
u_{31}	C(44)-C(45)	155.7(1)	4.2(*tied to* u_{28})		u_{100}	C(3)...C(44)	477.0(27)	12.1(*tied to* u_{93})	
u_{32}	C(3)-C(5)	155.7(1)	4.2(*tied to* u_{28})		u_{101}	C(19)...C(31)	478.4(36)	12.7(*tied to* u_{93})	
u_{33}	C(31)-C(33)	155.7(1)	4.2(*tied to* u_{28})		u_{102}	C(3)...C(47)	478.4(36)	12.7(*tied to* u_{93})	
u_{34}	C(44)-C(47)	155.7(1)	4.2(*tied to* u_{28})		u_{103}	C(17)...C(31)	480.8(59)	18.9(*tied to* u_{93})	
u_{35}	C(16)-C(19)	155.7(1)	4.2(*tied to* u_{28})		u_{104}	C(3)...C(45)	480.8(59)	18.9(*tied to* u_{93})	
u_{36}	C(16)-C(18)	155.7(1)	4.2(*tied to* u_{28})		u_{105}	C(16)...C(45)	490.7(44)	17.6(*tied to* u_{93})	
u_{37}	C(44)-C(46)	155.7(1)	4.2(*tied to* u_{28})		u_{106}	C(17)...C(44)	490.7(44)	17.6(*tied to* u_{93})	
u_{38}	C(31)-C(32)	155.7(1)	4.2(*tied to* u_{28})		u_{107}	C(4)...C(17)	506.8(24)	9.5(*tied to* u_{93})	

u_{39}	C(3)-C(4)	155.7(1)	4.2(*tied to* u_{28})		u_{108}	C(32)...C(45)	506.8(24)	9.5(*tied to* u_{93})		
u_{40}	Si(2)...C(47)	425.2(34)	15.2(18)	15.5(16)	u_{109}	C(5)...C(32)	564.1(34)	22.7(*tied to* u_{93})		
u_{41}	Si(1)...C(19)	425.2(34)	15.2(*tied to* u_{40})		u_{110}	C(6)...C(33)	580.4(38)	28.1(34)	25.6(26)	
u_{42}	Si(2)...C(33)	511.1(16)	19.1(21)		u_{111}	C(34)...C(47)	493.9(31)	21.5(*tied to* u_{110})		
u_{43}	Si(1)...C(18)	501.6(15)	11.7(*tied to* u_{42})		u_{112}	C(6)...C(19)	493.9(31)	21.5(*tied to* u_{110})		
u_{44}	Si(2)...C(46)	501.6(15)	11.7(*tied to* u_{42})		u_{113}	C(33)...C(45)	502.3(28)	18.4(*tied to* u_{110})		
u_{45}	Si(1)...C(5)	511.1(16)	19.1(*tied to* u_{42})		u_{114}	C(5)...C(17)	502.3(28)	18.4(*tied to* u_{110})		
u_{46}	C(5)...C(6)	256.3(31)	10.5(9)		u_{115}	C(16)...C(44)	509.6(26)	15.3(*tied to* u_{110})		
u_{47}	C(46)...C(47)	246.3(30)	10.4(*tied to* u_{46})		u_{116}	C(19)...C(32)	542.4(48)	19.2(*tied to* u_{110})		
u_{48}	C(18)...C(19)	246.3(30)	10.4(*tied to* u_{46})		u_{117}	C(4)...C(47)	542.4(48)	19.2(*tied to* u_{110})		
u_{49}	C(4)...C(6)	249.9(26)	10.2(*tied to* u_{46})		u_{118}	C(16)...C(32)	552.0(32)	20.3(*tied to* u_{110})		
u_{50}	C(32)...C(34)	249.9(26)	10.2(*tied to* u_{46})		u_{119}	C(4)...C(44)	552.0(32)	20.3(*tied to* u_{110})		
u_{51}	C(4)...C(5)	250.4(25)	10.5(*tied to* u_{46})		u_{120}	C(5)...C(34)	580.4(38)	28.1(*tied to* u_{110})		
u_{52}	C(32)...C(33)	250.4(25)	10.5(*tied to* u_{46})		u_{121}	C(5)...C(31)	585.3(32)	23.5(*tied to* u_{110})		
u_{53}	C(17)...C(18)	250.9(23)	10.3(*tied to* u_{46})		u_{122}	C(3)...C(33)	585.3(32)	23.5(*tied to* u_{110})		
u_{54}	C(45)...C(46)	250.9(23)	10.3(*tied to* u_{46})		u_{123}	C(34)...C(46)	522.1(34)	26.6(22)	18.7(20)	
u_{55}	C(45)...C(47)	254.9(25)	10.6(*tied to* u_{46})		u_{124}	C(6)...C(18)	522.1(34)	26.6(*tied to* u_{123})		
u_{56}	C(17)…C(19)	254.9(25)	10.6(*tied to* u_{46})		u_{125}	C(6)...C(17)	560.1(18)	19.3(*tied to* u_{123})		
u_{57}	C(33)...C(34)	256.3(31)	10.5(*tied to* u_{46})		u_{126}	C(34)...C(45)	560.1(18)	19.3(*tied to* u_{123})		
u_{58}	C(4)...C(32)	364.5(43)	46.5(*tied to* u_{46})		u_{127}	C(17)...C(46)	571.2(35)	31.5(*tied to* u_{123})		
u_{59}	C(4)...C(19)	338.9(40)	14.4(18)	14.8(15)	u_{128}	C(18)...C(45)	571.2(35)	31.5(*tied to* u_{123})		
u_{60}	C(32)...C(47)	338.9(40)	14.4(*tied to* u_{59})		u_{129}	C(17)...C(33)	576.4(59)	46.5(*tied to* u_{123})		
u_{61}	C(3)...C(19)	346.9(34)	14.9(*tied to* u_{59})		u_{130}	C(5)...C(45)	576.4(59)	46.5(*tied to* u_{123})		
u_{62}	C(31)...C(47)	346.9(34)	14.9(*tied to* u_{59})		u_{131}	C(18)...C(34)	586.0(35)	30.2(*tied to* u_{123})		
u_{63}	C(33)...C(44)	354.9(29)	14.8(*tied to* u_{59})		u_{132}	C(6)...C(46)	586.0(35)	30.2(*tied to* u_{123})		
u_{64}	C(5)...C(16)	354.9(29)	14.8(*tied to* u_{59})		u_{133}	C(4)...C(45)	589.1(56)	38.2(*tied to* u_{123})		
u_{65}	C(33)...C(47)	378.8(48)	22.4(*tied to* u_{59})		u_{134}	C(17)...C(32)	589.1(56)	38.2(*tied to* u_{123})		
u_{66}	C(5)...C(19)	378.8(48)	22.4(*tied to* u_{59})		u_{135}	C(5)...C(44)	603.7(32)	36.2(*tied to* u_{123})		
u_{67}	C(32)...C(44)	381.8(23)	9.8(*tied to* u_{59})		u_{136}	C(16)...C(33)	603.7(32)	36.2(*tied to* u_{123})		
u_{68}	C(4)...C(16)	381.8(23)	9.8(*tied to* u_{59})		u_{137}	C(19)...C(33)	610.5(45)	35.7(*tied to* u_{123})		

[a] Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses.

[b] Amplitudes not refined were fixed at the values obtained using the HF/6-31G* force field.

[c] C-H amplitude (u_{147}) was also refined: r_a = 113.6 pm, u = 6.0(1) pm, with u_{148}-u_{182} (all C-H) tied to u_{147}.

Table S3 Least squares correlation matrix (× 100) for the GED refinement of 1,1,2,2-tetra-*tert*-butyldisilane.[a]

	p_5	p_7	p_8	p_{16}	p_{17}	p_{18}	p_{22}	p_{23}	p_{31}	u_{36}	u_{182}	u_{183}
p_2		56										59
p_4	-99											
p_{10}				61	61							
p_{21}												-60
p_{17}				56								
p_{18}				-73								
p_{23}												
p_{24}						50	-53					
p_{25}											60	
p_{29}			-57					-50				
p_{30}									-61			
k_2										53		

[a] Only elements with absolute values ≥ 50% are shown; k_2 is a scale factor.

Table S4 Experimental gas electron diffraction coordinates from the refinement of 1,1,2,2-tetra-*tert*-butyldisilane.

Atom Number	*x*	*y*	*z*
Si(1)	-1.2261	0.0000	0.0000
Si(2)	1.2261	0.0000	0.0000
C(3)	2.1096	-0.6311	1.6121
C(4)	1.8152	-2.1091	1.9971
C(5)	3.6515	-0.4869	1.4681
C(6)	1.5681	0.2589	2.7670
H(7)	1.7824	-2.7984	1.0955
H(8)	2.6361	-2.4454	2.7059
H(9)	0.8143	-2.1321	2.5328
H(10)	4.0349	-1.4117	0.9324
H(11)	3.9524	0.4425	0.8894

H(12)	4.0879	-0.4432	2.5154
H(13)	0.4492	0.4380	2.6944
H(14)	1.8083	-0.2684	3.7435
H(15)	2.1179	1.2514	2.7231
C(16)	1.9124	-0.8406	-1.6125
C(17)	0.8962	-0.5351	-2.7497
C(18)	3.3208	-0.4041	-2.1076
C(19)	2.0254	-2.3756	-1.3886
H(20)	-0.0233	-1.1767	-2.5707
H(21)	0.5972	0.5596	-2.7876
H(22)	1.3848	-0.8322	-3.7306
H(23)	3.1925	0.5465	-2.7151
H(24)	4.0466	-0.2177	-1.2546
H(25)	3.7185	-1.2330	-2.7739
H(26)	1.2241	-2.7767	-0.6912
H(27)	1.9331	-2.8747	-2.4042
H(28)	3.0523	-2.5848	-0.9516
H(29)	1.7517	1.4219	0.0000
H(30)	-1.7517	-0.2323	-1.4028
C(31)	-2.1096	-1.4874	0.8860
C(32)	-1.8152	-1.6258	2.4069
C(33)	-3.6515	-1.3688	0.7202
C(34)	-1.5681	-2.7722	0.1965
H(35)	-1.7824	-0.6237	2.9398
H(36)	-2.6361	-2.2701	2.8545
H(37)	-0.8143	-2.1505	2.5172
H(38)	-4.0349	-0.6893	1.5451
H(39)	-3.9524	-0.9497	-0.2913
H(40)	-4.0879	-2.4092	0.8481
H(41)	-0.4492	-2.7297	0.0080
H(42)	-1.8083	-3.6493	0.8763
H(43)	-2.1179	-2.8910	-0.7898
C(44)	-1.9124	1.7282	0.5659
C(45)	-0.8962	2.8002	0.0788
C(46)	-3.3208	2.1453	0.0545
C(47)	-2.0254	1.7579	2.1169
H(48)	0.0233	2.7284	0.7410
H(49)	-0.5972	2.6587	-1.0074
H(50)	-1.3848	3.8165	0.2117
H(51)	-3.1925	2.5894	-0.9826
H(52)	-4.0466	1.2733	0.0099
H(53)	-3.7185	2.9380	0.7634
H(54)	-1.2241	1.1354	2.6265
H(55)	-1.9331	2.8415	2.4434
H(56)	-3.0523	1.3610	2.3946