Supplementary information

1,4-Disilacyclohexa-2,5-diene: A Molecular Building Block that Allows for Remarkably Strong Neutral Cyclic Cross-Hyperconjugation

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Contents:

Experimental details

General Remarks: The starting materials and cyclohexa-1,4-diene (**6**) were commercially available, as were the solvents used. All chemicals and solvents were used as purchased except THF which was dried over sodium with sodium benzophenone ketyl as indicator and freshly distilled before usage. All reactions were perfomed under inert atmosphere (N_2 or Ar).

The ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Unity 400 MHz (399.97 MHz for ^1H, 100.57 MHz for ^{13}C and 80 MHz for ^{29}Si) spectrometer. The ^{29}Si spectra were measured using the selective INEPT technique, with a simultaneous magnetization transfer from surrounding protons to the Si nuclei. Chemical shifts are reported in ppm, referenced to the residual solvent peak ($CHCl_3$). Mass spectra (m/z (relative intensity, %)) were obtained using a Finnigan MAT GCQ PLUS instrument (EI mode, 70 eV). An FT-IR spectrometer with ATR accessory was used, and IR frequencies are reported as ($\tilde{\nu}$ / cm^{-1}, relative intensity).

Ultraviolet photoelectron spectroscopy: The photoelectron spectra were recorded using a conventional electron spectrometer.[1] The HeIα line at 21.22 eV, obtained from a gas discharge lamp, was used for ionization. Spectra were recorded with an overall resolution of about 30 meV. For calibration purposes of the binding energy scale, a mixture of the sample gas and Ar with well-known 3p lines at 15.760 and 15.937 eV was used.[2]

Cyclic Voltammetry: Electrochemical data were obtained by cyclic voltammetry using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie) and a standard three-electrode setup. A glassy carbon disc electrode was used as the working electrode, a platinum wire as counter electrode and a non-aqueous Ag/Ag^+ electrode (10 mmol in CH_3CN) as a reference electrode. CVs of 1 mM solutions of the analytes in CH_2Cl_2 (containing 0.1 M NBu_4PF_6 as supporting electrolyte) were run with a scan rate of 100 mV/s. All potentials are given *versus* the Fc/Fc^+ couple, which was added after each experiment as internal standard.

Computational methods: All calculations were performed with the Gaussian 03 and 09 program packages.[3,4] The geometry optimizations were done at the B3LYP hybrid density functional theory (DFT) level,[5] with the 6-31G(d) valence double-zeta basis set of Pople and Hariharan.[6] The stationary points were subjected to frequency calculations to examine their characters as minima or saddle points. A few of the compounds were also examined at the M06-2X/6-311G(d)[7,8] hybrid meta DFT level as well as at the MP2/6-31G(d), or CCSD/6-311G(d) levels.

In order to evaluate vertically excited states, time-dependent DFT (TD-DFT) calculations were carried out on the optimal B3LYP/6-31G(d) geometries. The TD-DFT calculations were performed with the PBE0 hybrid functional using the 6-31+G(2d) basis set.[9-12]

The vertical ionization potentials (IPs) were calculated using Cederbaum’s outer valence Green’s function (OVGF) method,[13] with the 6-311+G(d) basis set.[14] In the OVGF treatment of **1b-I** the occupied molecular orbital number 15 until LUMO (MO number 53), and for **1c-I** the window of the OVGF calculation included the occupied MO number 23 until LUMO (MO number 89).

Geometry optimazations of the model compounds **11-14** were performed on C_2 symmetric molecules in which only the dihedral angles ω had been constrained (0° - 180° with 10° increments). These geometries were then used for the properties calculations.

X-ray crystallographic analysis: Colourless crystals of **1c** were obtained by recrystallization from diethylether. For X-ray structure analysis, the crystal was mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F^2_o and corrected for absorption effects with SAINT and SADABS, respectively. The structure was solved by direct methods and refined by full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the calculated positions corresponding to standard bond lengths and angles. Crystallographic data (excluding structure factors) for **1c** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 775978. Copies of the data can be obtained free of charge on application at www.ccdc.cam.ac.uk/products/csd/request.

Syntheses of 1a – 1c:

Synthesis of 1,1,4,4-tetrachloro-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene (**1a**): A sealed glass ampoule containing trichlorosilane (30.28 g, 223.60 mmol), 3-hexyne (5.50 g, 67.00 mmol) and tetrabutyl phosphonium chloride (2.00 g, 6.70 mmol) was heated to 180 °C for 10 hours in a stainless steel bomb. The excess of the starting material was then removed under reduced pressure. The product was distilled yielding 75 % (18.20 g, 50.30 mmol) of the title compound previously reported by Jung's group.[15] UV (gas phase, 1.67×10^{-5} mol/L) λ_{max} / nm ($\varepsilon \times 10^4$ dm^3 mol^{-1} cm^{-1}) 198.1 (1.45).

Synthesis of 2,3,5,6-tetraethyl-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (**1b**): To **1a** (18.21 g, 50.31 mmol) dissolved in THF (240 ml) and cooled to -78 °C, MeLi (300 mmol, 1.6 mol/L) was added over 2 hours. The reaction mixture was then allowed to reach room temperature over night. The reaction was then quenched by addition of water (50 ml) and the phases were separated. The organic phase was washed with water (3 × 25 ml) and brine 15 ml. After removal of the solvent, the obtained product was purified on a plug of silica with neat pentane as eluent. The pentane was removed and the product was further purified by distillation at 2 mbar and 68 °C (which is similar to previously reported b.p.)[16] resulting in 75 % (10.59 g, 37.73 mmol) of the desired product **1b**. ^{1}H NMR ($CDCl_3$) δ: 0.14 (s, 12H, 2xSi(C**H**$_3$)$_2$), 0.98 (t, ^3J = 7.64 Hz, 12H, 4xCH$_2$C**H**$_3$), 2.26 (q, ^3J = 7.64 Hz, 8H, 4xC**H**$_2$CH$_3$) ppm. ^{13}C δ: -0.9 (Si(**C**H$_3$)$_2$), 15.1 (**C**H$_2$), 23.7 (CH$_2$**C**H$_3$), 154.1 (C=C) ppm. ^{29}Si δ: -7.56 ppm EI-MS: 280 (29.1), 265.1 (100), 252.5, (19.9). IR: 811.31, 1244.31, 1409.31, 2962.53. UV (gas phase, 240 → 340 °C, 1.92×10^{-5} mol/L) λ_{max}/nm ($\varepsilon \times 10^4$ dm^3 mol^{-1} cm^{-1}) 196.2 (1.24). Anal. $C_{16}H_{32}Si_2$ (280.60 g/mol): Calc. C, 68.49; H, 11.49. Found C, 68.16; H, 11.47.

Synthesis of 2,3,5,6-tetraethyl-1,1,4,4-tetrakis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**1c**): To a mixture of **1a** (0.50 g, 1.38 mmol) and TMSCl (2.81 ml, 22.08 mmol) in THF (15 ml) Li (0.075 g, 11.04 mmol) was added at -78 °C. The reaction mixture was allowed to reach room temperature over night upon continued stirring. After 22 hours, more TMSCl (1.00 ml, 7.88 mmol) was added and the reaction mixture was stirred for additional 90 min. Thereafter, all volatile substances were removed under reduced pressure. The remaining solid material was dissolved in DCM (15 ml) and washed with water (3 × 10 ml). The organic phase was dried over $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator. The product was first purified by column chromatography with neat pentane as eluent. Thereafter, the product was distilled under reduced pressure (68 °C) and subsequently re-crystallized in hexane, yielding 71 % of **1c** (0.54 g, 1.97 mmol) as white crystals (m.p. 167 - 168 °C). ^{1}H NMR ($CDCl_3$) δ: 0.19 (s, 36H, 4xSi(C**H**$_3$)$_3$), 1.01 (t, ^{3}J = 7.47 Hz, 12H, 4xCH$_2$C**H**$_3$), 2.12 (q, ^{3}J = 7.47 Hz, 8H, 4xC**H**$_2$CH$_3$) ppm. ^{13}C δ: 1.1 (Si(**C**H$_3$)$_2$), 15.3 (**C**H$_2$), 26.0 (CH$_2$**C**H$_3$), 151.1 (C=C) ppm. ^{29}Si δ: -22.6 (**Si**(SiMe$_3$)$_2$), 121.3 (Si(**Si**Me$_3$)$_2$) ppm EI-MS: 512.30 (15.1), 439.2 (74.8), 365.3, (100), 74.49 (38.3). IR: 683.1, 742.6, 812.4, 1242.8, 2893.2, 2954.9. UV/Vis (cyclohexane, 2.07×10^{-5} mol/L) λ_{max}/nm ($\varepsilon \times 10^{4}$ dm^{3} mol^{-1} cm^{-1}) 237 (1.81) 273 (2.13). UV (gas phase, 250 → 350 °C, 3.70×10^{-5} mol/L) λ_{max}/nm ($\varepsilon \times 10^{4}$ dm^{3} mol^{-1} cm^{-1}) 194.4 (2.60), 214.0 (2.52), 273 (1.62). Anal. $C_{24}H_{56}Si_6$ (513.21 g/mol): Calc. C, 56.17; H, 11.00. Found C, 55.88; H, 10.82.

Gas phase UV absorption spectroscopy: The gas phase UV absorption spectra were measured on a modified Varian 300 spectrophotometer in which the standard track had been replaced by a system that was possible to heat to the boiling points of the variously investigated compounds. The stray-light of the UV-spectrophotometer was measured to be less than 0.1% of the total light beam. All UV absorption measurements were performed in dark. The temperature gradients for **1a** and **1b** went from 240 °C (bottom) to 340 °C (top), and for **1c** from 250 °C at the bottom to 350 °C at the top. The gas phase UV absorption measurement of **6** was performed at room temperature.

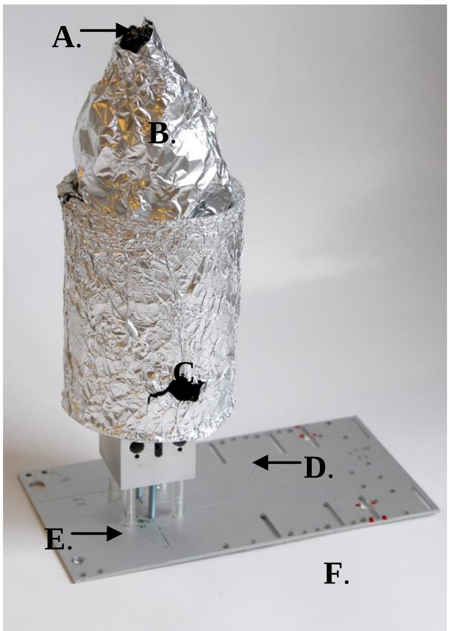
Measurements of compounds **1a** – **1c** was performed as follows; the sample was placed at the bottom of a ~70 mL cuvette, which was placed in liquid nitrogen and the atmosphere was changed to argon. The cuvette was melted off under vacuum and then placed in the UV-spectrophotometer where a background chromatogram was collected at room temperature. The bottom part of the cuvette was thereafter heated to ensure that the product remained in the gaseous phase to allow it to be detected by the UV-beam. After five minutes no signal was detected due to that the sample resided above the UV-beam. The top heater was then set to a temperature 100 °C above that of the bottom, forcing a convection current inducing a uniform sample distribution throughout the vessel so that the sample could be detected. To allow for determination of the molar extinction coefficient, the top of the cuvette was carefully removed with a grinder after each experiment and the exact volume of the cuvette was calculated by the maximum mass of water that was possible to add to the cuvette. The total time for a measurement was 12 minutes or less. The stabilities of the compounds **1a** – **1c** were tested in long-term measurements and peaks from degradation products of the compounds were visible in the UV absorption spectra after 45 min (**1a**), 3 h (**1b**) and 2 h (**1c**).

Reference compound, cyclohexa-1,4-diene, **6** was purchased and used without further purifications. Gas phase UV spectroscopy (room temperature, 2.89×10^{-4} mol/L) resulted in no well-defined peaks with weak absorption up to ~220 nm. The low vapor pressure allowed measurements at room temperature, and a different method was used to perform the measurements compared to **1a** – **1c**. First a spectrum of the empty cuvette was recorded as preliminary background, and thereafter the sample was prepared as described above, and left for 0.5 hours. A UV spectrum with weak absorption data was thereafter collected of **6**. The bottom of the cuvette was heated to 60 °C, and after 0.5 hours a new spectrum was collected containing no spectral data, which was used as the true background. The heating was turned off and the system was left for four hours until the final spectrum was collected.

Description of the setup for gas phase UV absorption spectroscopy

Photograph 1 shows the heating apparatus for the gas phase UV-measurements with the different parts labeled. The heating apparatus was placed in the UV/vis-spectrophotometer (Varian Cary 3 Bio UV-visible spectrophotometer), instead of in the ordinary cuvette rack.

On the heating block (Photograph 2, Scheme 1) a can in stainless steal (**C**, Scheme 2) with walls of 2 mm, coated in aluminum foil served as housing for the cuvette (Photograph 3, Scheme 3). The temperature of the air leaving the can from the opening (**D**) in the wall is defined as the top temperature. The temperature was measured with a thermocouple, K-type. On the top of the can, a cone (**B**) of aluminum foil with a small orifice (**A**) at the top was constructed to allow hot air from a heat gun to enter.



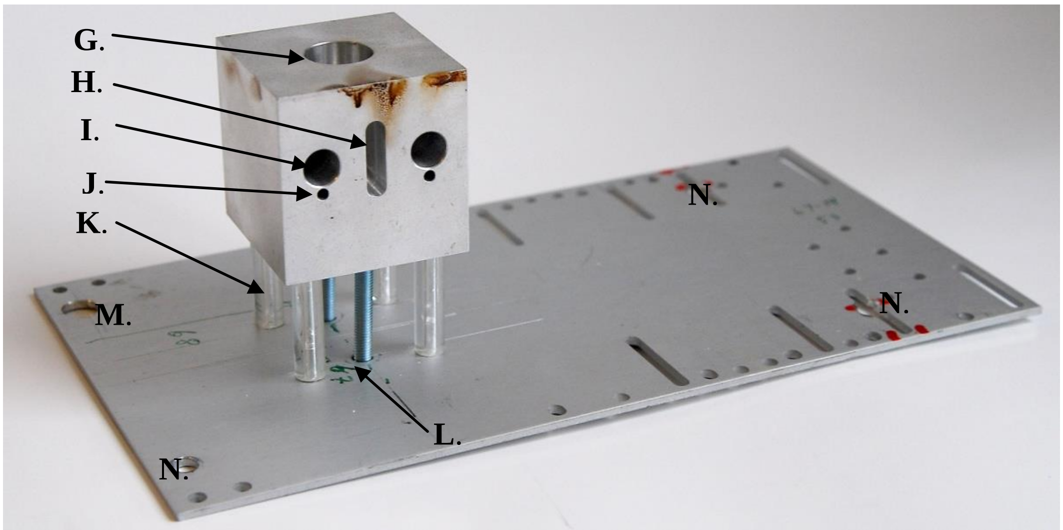
The heating apparatus:

- **A.** The orifice where warm air was blown in.
- **B.** The top cone.
- **C.** The stainless steel can (Scheme 2).
- **D.** The orifice where the air left the can.
- **E.** The heating aluminium block (Photograph 2, Scheme 1).
- **F.** The bottom plate (Photograph 2, Scheme 1).

Photograph 1. Complete heating device used in the gas phase UV experiments which was placed in the UV-spectrometer.

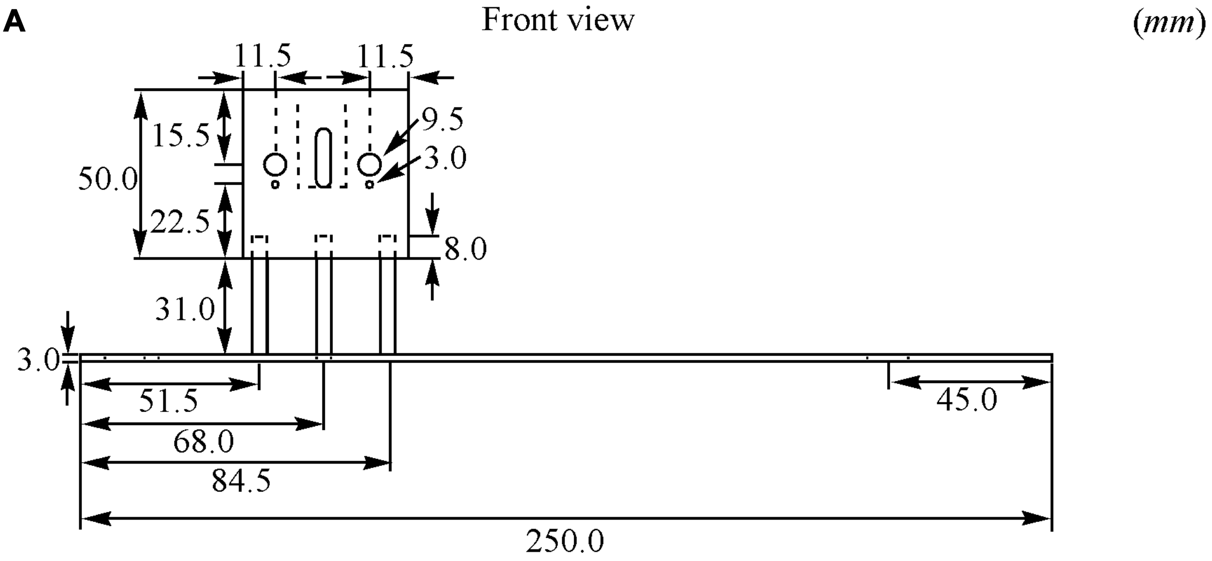
The heating block and the bottom plate were made of aluminum, with borosilicate glass legs (**K**). The two screws (**L**) of 5 mm diameter were used to support the heating block to the bottom plate, with a corresponding thread size in the aluminum block. The light beam passed through the heating block through opening **H** and the bottom of opening **G** where the cuvette (photography 2, Scheme 4) was placed. The bottom plate was sealed to the spectrophotometer with the three screws from the cuvette rack in openings (**N**) and the guiding nut was placed in opening (**M**). The other openings in the bottom plate were there to allow ventilation in the spectrophotometer. No parts or surfaces of the spectrophotometer became warmer than 35 °C.

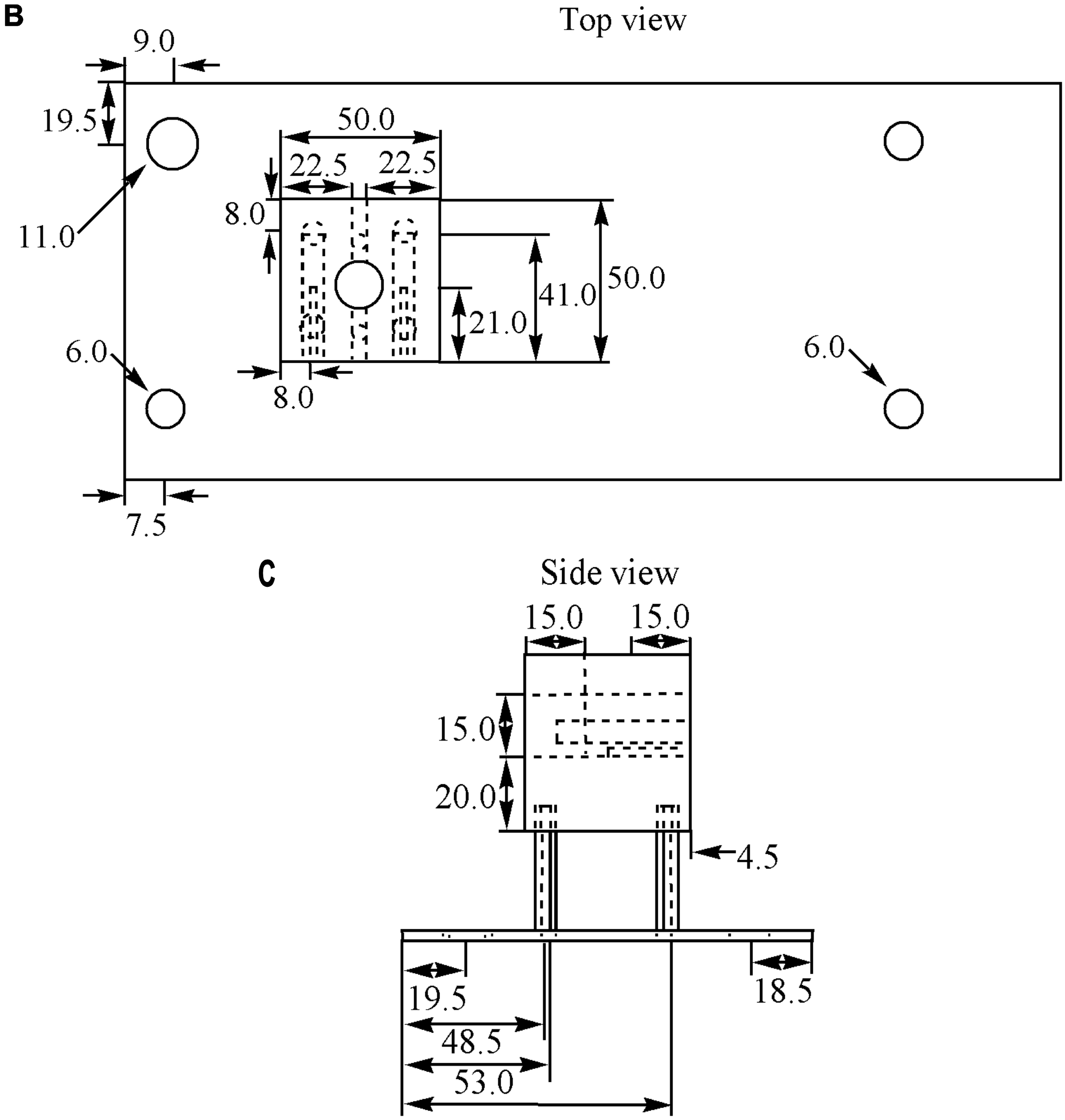
The rod-shaped heating elements from the injector of a Varian 3400 gas chromatograph were placed in the two larger circular openings (**I**) in the heating block. Since the GC only has one heating rod of 40 mm, the second heating rod in the GC is larger (at the detector) and was therefore exchanged to an injector rod from another similar GC. In the two smaller openings (**J**), the GC:s temperature sensors were placed. The temperature given by the GC sensors is defined as the bottom temperature in the paper.



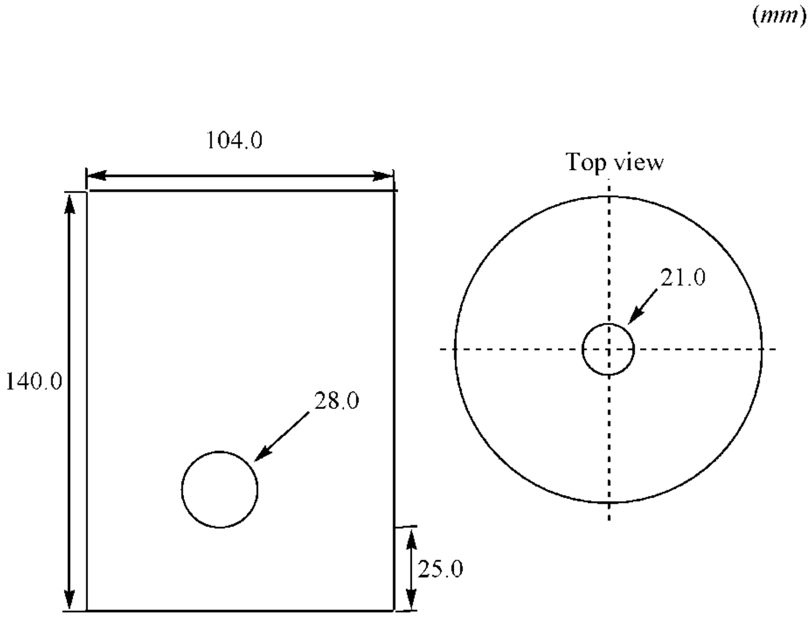
G. Cuvette holder. **H.** Slit. **I.** Position for heating element. **J.** Position for heating sensor. **K.** Borosilicate leg. **L.** Support screws that hold heating block to the bottom plate. **M**. Opening for guiding nut. **N.** Positions for anchoring the heating device to the spectrometer.

Photograph 2. The heating block and the bottom plate.





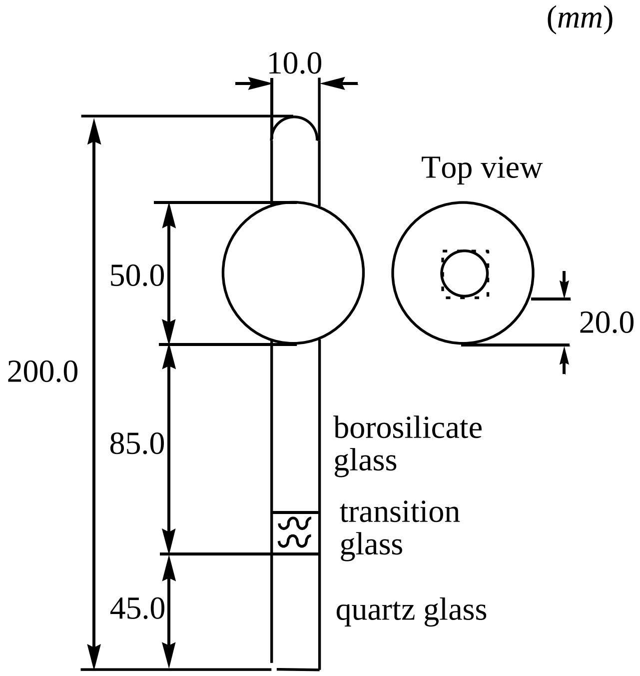
Scheme S1. **A.** Front view, **B.** Top view. **C.** Side view of the heating block and the bottom plate. All vertical and horizontal arrows refer to the respective distances, and all diagonal arrows refer to diameters of circular openings.



Scheme S2. The representation of the top cone (**C**) in Photograph 1. All vertical and horizontal arrows refer to the respective distances, and all diagonal arrows refer to diameters of circular openings.

Photograph and schematic drawing of gas phase cuvette

Photograph 3. Gas cuvette



Scheme S3. Dimensions of the gas cuvette.

Molecular orbitals

The occupied group orbital of b_{1u} symmetry on the 2x(C=C) fragment and the two occupied and unoccupied group orbitals of this symmetry on 2x(SiR_2) combine into the three $1b_{1u}$, $2b_{1u}$, and $3b_{1u}$ MOs of which the first two are occupied. Similarly, the vacant b_{2g} group orbital of 2x(C=C) combine with the two b_{2g} orbitals of the 2x(SiR_2) fragment into the $1b_{2g}$, $2b_{2g}$, and $3b_{2g}$ MOs, where the first one is occupied. One b_{1u} and one a_u orbital also exist on the 2x(C=C) fragment, but neither of these can interact with a suitable π-symmetric orbital at 2x(SiR_2) constructed from two π(SiR_2) or two π*(SiR_2) orbitals. They may instead each interact with the two empty 3d(Si) AOs combined into b_{3g} and a_u symmetric 2x(SiR_2) group orbitals. The interaction between the occupied b_{3g} group orbital of the 2x(C=C) fragment and the vacant b_{3g} orbital of 2x(SiR_2) should be negligible so that the $1b_{3g}$ MO remains localized to the two C=C double bonds. However, the interaction between the vacant a_u group orbital of 2x(C=C) and the vacant a_u orbital of 2x(SiR_2) can, on the other hand, be substantial .

The LUMO of **1c** also has an interesting character since it is the 1a symmetric MO ($1a_u$ in D_{2h}) which corresponds to an interaction between the a (a_u) symmetric combination of π^*_{CC} at 2x(C=C) with the a (a_u) symmetric combination of the two 3d(Si) AO of 2x(SiR_2) (Figure S1).Hence, this orbital shows that empty 3d(Si) AOs can contribute to the lowest unoccupied MOs when there are suitable local orbitals on adjacent molecular segments to interact with.The contribution of 3d(Si) AOs to LUMO is noteworthy because d-AO participation is generally regarded as negligible in the bonding of the heavy main group element compounds in their electronic ground states.[17,18]

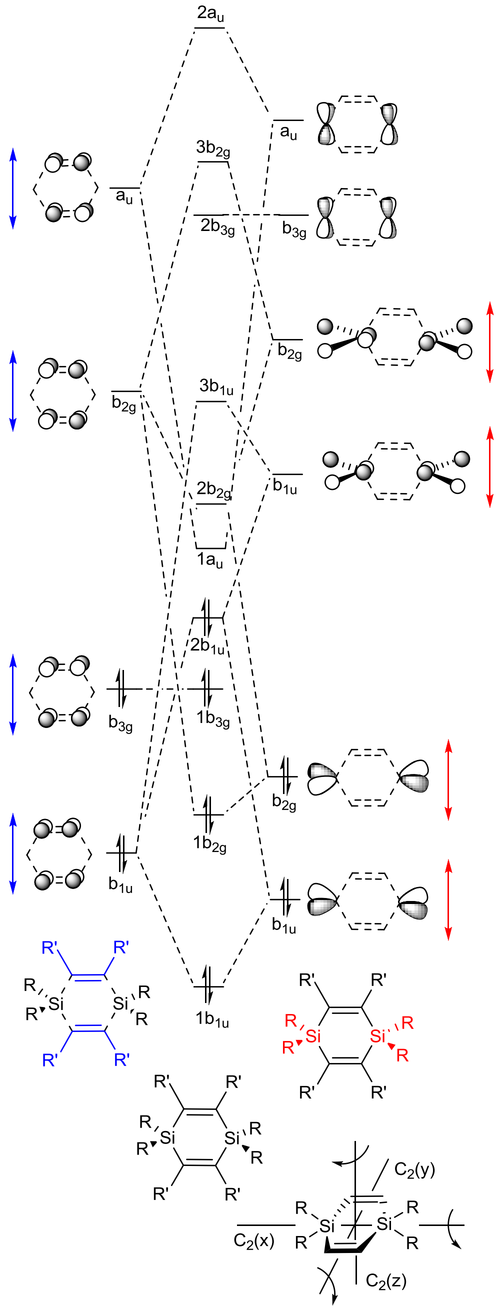


Figure S1. Qualitative molecular orbital (MO) diagram of D_{2h} symmetric 1,4-disilacyclohexa-2,5-diene with the lowest few occupied and unoccupied MOs of π-character constructed from suitable fragment orbitals. Red arrows indicate changes in fragment orbital energies in dependence of substituents R and blue arrows indicate changes of substituents R'. The orbitals are labelled in accordance with the irreducible representations of the D_{2h} point group. The three C_2 rotational axes are arranged as shown in the structure in the lower right corner.

Orbital plots

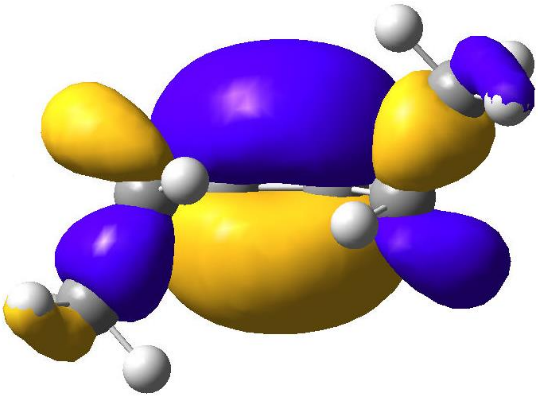


Figure S2. HOMO of the 3-hexene fragment calculated to -6.40 eV at B3LYP/6-31G(d) level.

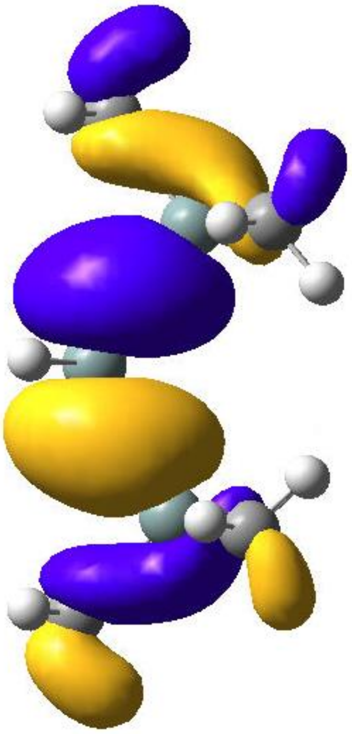


Figure S3. The π(SiR_2) orbital (HOMO) of the $H_2Si(SiMe_3)_2$ fragment calculated to -6.53 eV at B3LYP/6-31G(d) level.

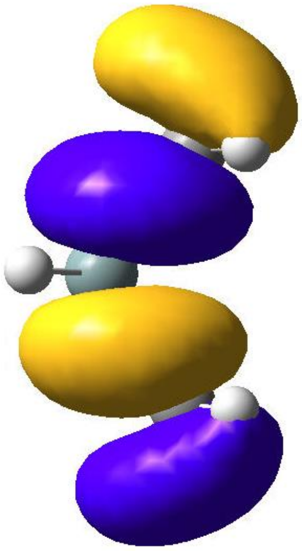


Figure S4. The π(SiR$_2$) orbital (HOMO) of the H$_2$SiMe$_2$ fragment calculated to -8.38 eV at B3LYP/6-31G(d) level.

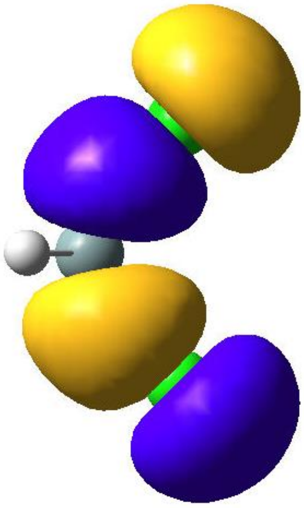


Figure S5. The π(SiR$_2$) orbital (HOMO-6) of the H$_2$SiCl$_2$ fragment calculated to -11.45 eV at B3LYP/6-31G(d) level.

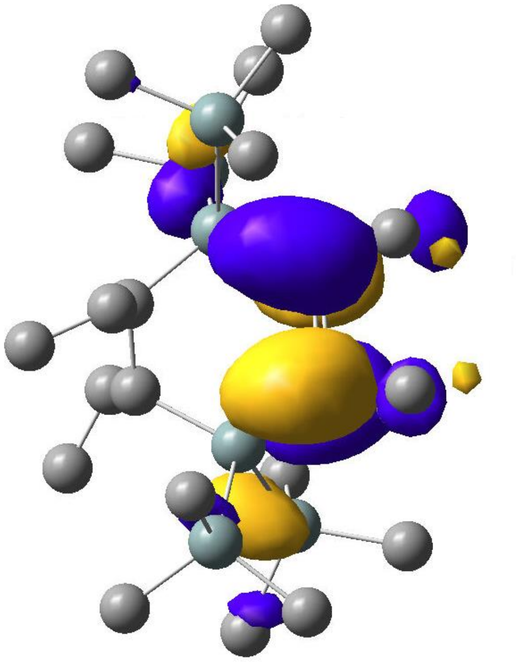


Figure S6. LUMO of **7** calculated to -0.27 eV at B3LYP/6-31G(d) level**.** Hydrogens omitted for clarity.

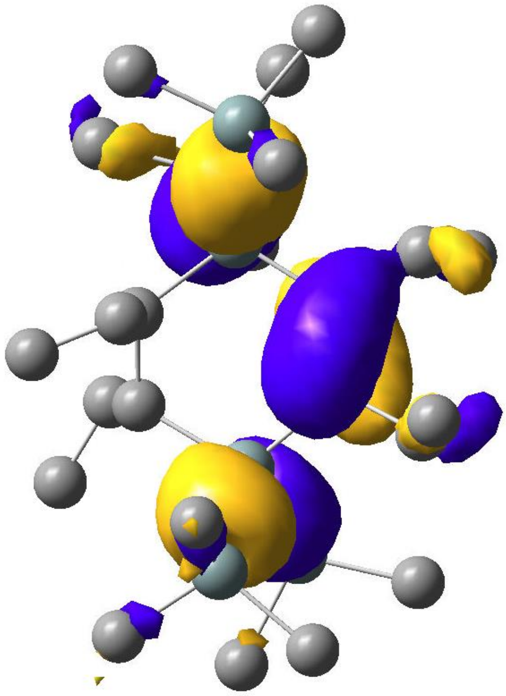
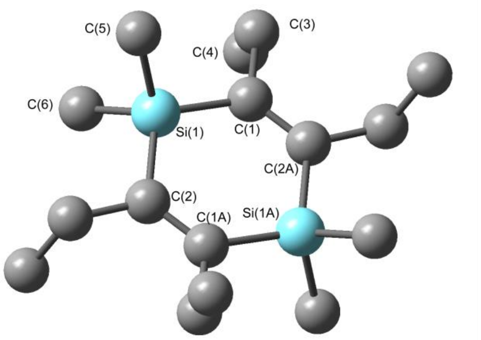
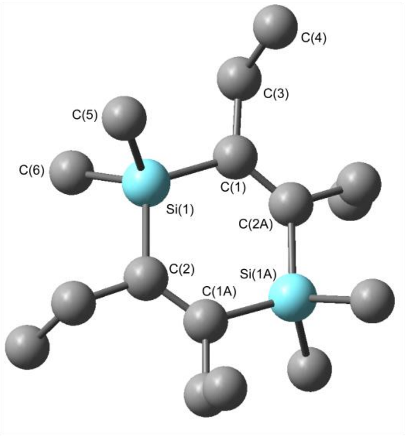


Figure S7. HOMO of **7** calculated to -5.50 eV at B3LYP/6-31G(d) level. Hydrogens omitted for clarity.

Geometric structure: The most important calculated geometry parameters of **1a** and **1b** are similar to those of **1c**, and for both compounds conformers of type-**I** are more stable than those of type-**II** by 0.4 – 1.0 kcal/mol at B3LYP/6-31G(d) as well as MP2/6-31G(d) levels. For **1a** this relative stability between the two conformer types agrees with the previously determined X-ray crystal structure which was found by Jung and co-workers[15] to correspond to the **1a-I** conformer. The calculated C=C double bonds in both **1a-I** and **1b-I** are minutely shorter than those of **1c-I** (Figure **S8**).



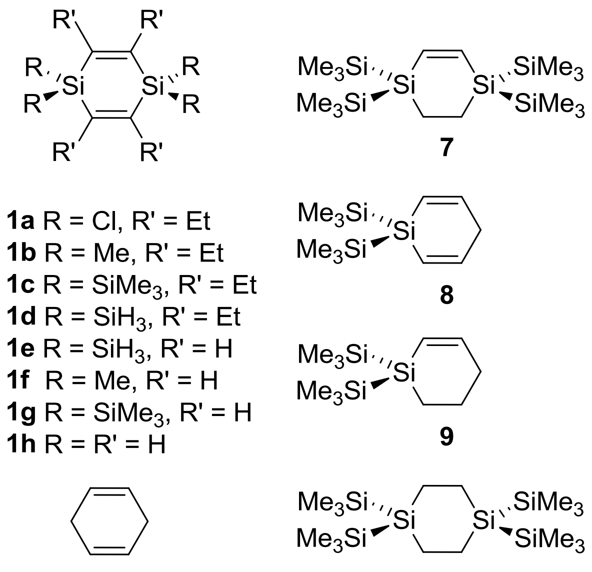
1b-I



1b-II

Figure S8. Optimized B3LYP/6-31G(d) geometries of **1b-I** (normal print) and **1b-II** (italics). Selected bond lengths (Å) and angles (deg), the hydrogen atoms are omitted for clarity: Si(1)-C(1) 1.890 (*1.891*), Si(1)-C(5) 1.902 (*1.903*), Si(1)-C(6) 1.903 (*1.903*), C(1)-C(2A) 1.357 (*1.358*), C(2)-C(5) 1.531 (*1.532*), C(3)-C(4) 1.542 (*1.542*), C(7)-Si(1)-Si(6) 106.54 (*106.90*), Si(1A)-Si(1)-C(5) 132.65 (*131.77*), Si(1A)-Si(1)-C(6) 120.80 (*121.33*), C(5)-Si(1)-C(1) 110.56 (*110.42*), C(6)-Si(1)-C(1) 107.77. (*110.14*), C(5)-Si(1)-C(6) 113.33 (*112.98*), Si(1)-C(1)-C(3) 114.92 (*115.43*), Si(1)-C(1)-C(2A) 123.02 (*123.43*), C(1)-Si(1)-C(2)-C(1A) 9.74 (*1.00*), Si(1)-C(1)-C(2)-Si(1A) 8.88 (*9.01*).

Analysis of the impact of steric congestion on 1,4-disilacyclohexa-2,5-diene geometries: The 1,4-disilacyclohexa-2,5-dienes with silyl (**1d**, Scheme S4) instead of TMS groups at Si as in **1c** has somewhat shorter Si-Si bonds (2.373 vs 2.400 Å in **1c**) as the steric bulk is decreased. The C=C double bonds are somewhat shortened (1.358. *vs*, 1.361 Å) and the Si-C bonds are likewise shorter (1.894 *vs* 1.908 Å). Removing the ethyl groups, as in **1e**, further shortens the Si-Si bonds to 2.363 Å and the C=C bonds to 1.350 Å. The Si-C bonds are 1.883 Å as a result of the reduced steric bulk. Probing the effect of the silyl substituents in **1e** by replacing these with methyl groups, **1f**, gives shortened C=C bonds to 1.347Å while the Si-C bond lengths are essentially unchanged. This indicate an slight effect of cross-hyperconjugation as the C=C of **1f** double bonds are shortened when compared to **1e**. See table S1 for summary of all results.

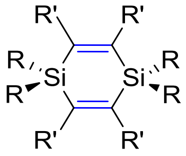


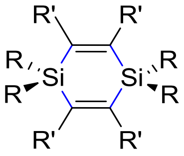
1a R = Cl, R' = Et
1b R = Me, R' = Et
1c R = SiMe$_3$, R' = Et
1d R = SiH$_3$, R' = Et
1e R = SiH$_3$, R' = H
1f R = Me, R' = H
1g R = SiMe$_3$, R' = H
1h R = R' = H

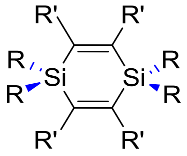
6 **7** **8** **9** **10**

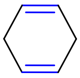
Scheme S4. The substituted 1,4-disilacyclohexa-2,5-dienes, the all-carbon reference, cyclohexa-1,4-diene, investigated and the derivatives of 1,4-disilacyclohexa-2-ene (**7-10**) investigated herein.

Table S1. Summary of the calculated geometries at B3LYP/6-31G(d) level.







Compound	$r_{C=C}$	$r_{Si\text{-}C}$	$r_{Si\text{-}R}$
1a R = Cl, R' = Et	1.359	1.871	2.093
1b R = Me, R' = Et	1.357	1.890	1.902
1c R = $SiMe_3$, R' = Et	1.361	1.908	2.400
1d R = SiH_3, R' = Et	1.358	1.894	2.373
1e R = SiH_3, R' = H	1.350	1.883	2.363
1f R = Me, R' = H	1.347	1.882	1.896
1g R = $SiMe_3$, R' = H	1.351	1.889	2.381
R = H R' = H	1.347	1.876	1.492
R = F R' = H	1.344	1.858	1.608
			
6 cyclohexa-1,4-diene	1.335	-	-

X-ray Crystallographic data

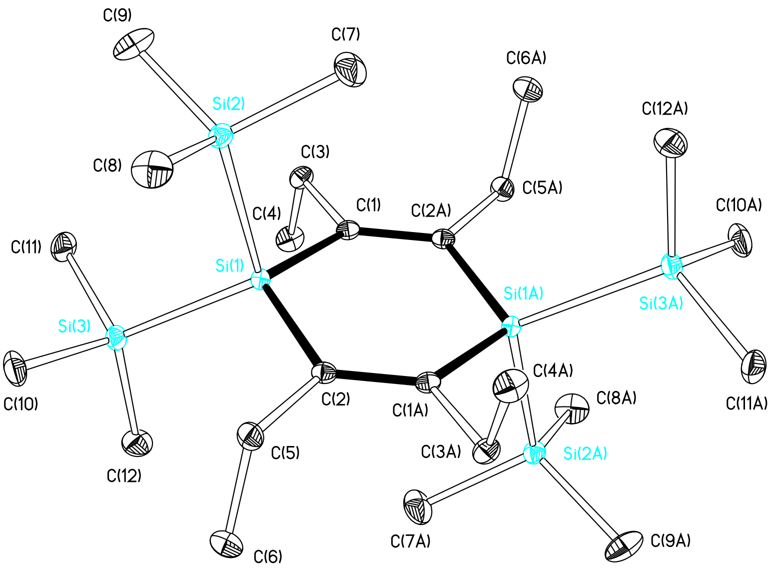


Table S2. Crystal data and structure refinement for **1c** (CCDC 775978).

Empirical formula	$C_{23.50}H_{56}Si_6$
Formula weight	507.22
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group Monoclinic,	C2/c
Unit cell dimensions	a = 17.135(3) Å alpha = 90 deg.
	b = 9.4044(19) Å beta = 101.54(3) deg.
	c = 20.723(4) Å gamma = 90 deg.
Volume	3271.9(11) $Å^3$
Z, Calculated density	4, 1.030 Mg/m^3
Absorption coefficient	0.265 mm^{-1}
F(000)	1124
Crystal size	0.34 x 0.28 x 0.20 mm
Theta range for data collection	2.01 to 26.79 deg.
Limiting indices	$-21 \le h \le 21, -11 \le k \le 11, -26 \le l \le 26$
Reflections collected / unique	12948 / 3486 [R(int) = 0.0268]
Completeness to theta = 26.79	99.6 %
Absorption correction	SADABS
Max. and min. transmission	0.9490 and 0.9154
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3486 / 0 / 144
Goodness-of-fit on F^2	1.070
Final R indices [I > 2sigma(I)]	R1 = 0.0311, wR2 = 0.0819
R indices (all data)	R1 = 0.0332, wR2 = 0.0837
Largest diff. peak and hole	0.416 and -0.169 e/$Å^3$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **1c**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Si(1)	1892(1)	7959(1)	4263(1)	13(1)
Si(2)	972(1)	6109(1)	3894(1)	18(1)
Si(3)	1683(1)	9844(1)	3489(1)	20(1)
C(1)	1693(1)	8447(1)	5097(1)	15(1)
C(2)	2883(1)	7051(1)	4330(1)	15(1)
C(3)	973(1)	9412(1)	5077(1)	19(1)
C(4)	1238(1)	10966(1)	5186(1)	25(1)
C(5)	3146(1)	6774(1)	3678(1)	21(1)
C(6)	3744(1)	7886(2)	3539(1)	29(1)
C(7)	1017(1)	4875(2)	4610(1)	40(1)
C(8)	1242(1)	5049(2)	3202(1)	33(1)
C(9)	-77(1)	6745(2)	3608(1)	36(1)
C(10)	1726(1)	9110(2)	2654(1)	31(1)
C(11)	663(1)	10655(2)	3410(1)	29(1)
C(12)	2426(1)	11333(2)	3682(1)	30(1)

Table S4. Bond lengths [Å] and angles [deg] for **1c**.

Si(1)-C(2)	1.8815(13)
Si(1)-C(1)	1.8845(13)
Si(1)-Si(2)	2.3685(6)
Si(1)-Si(3)	2.3690(6)
Si(2)-C(7)	1.8725(16)
Si(2)-C(9)	1.8753(16)
Si(2)-C(8)	1.8797(15)
Si(3)-C(10)	1.8781(15)
Si(3)-C(12)	1.8804(15)
Si(3)-C(11)	1.8836(15)
C(1)-C(2)#1	1.3456(18)
C(1)-C(3)	1.5254(16)
C(2)-C(1)#1	1.3456(18)
C(2)-C(5)	1.5297(16)
C(3)-C(4)	1.5335(18)
C(5)-C(6)	1.5307(19)
C(2)-Si(1)-C(1)	111.66(6)
C(2)-Si(1)-Si(2)	102.90(4)
C(1)-Si(1)-Si(2)	104.13(4)
C(2)-Si(1)-Si(3)	113.66(4)
C(1)-Si(1)-Si(3)	114.06(4)
Si(2)-Si(1)-Si(3)	109.33(3)
C(7)-Si(2)-C(9)	109.44(9)
C(7)-Si(2)-C(8)	107.41(8)
C(9)-Si(2)-C(8)	107.09(8)
C(7)-Si(2)-Si(1)	106.29(6)

C(9)-Si(2)-Si(1)	113.69(5)
C(8)-Si(2)-Si(1)	112.73(5)
C(10)-Si(3)-C(12)	108.62(7)
C(10)-Si(3)-C(11)	105.93(8)
C(12)-Si(3)-C(11)	107.12(7)
C(10)-Si(3)-Si(1)	108.64(5)
C(12)-Si(3)-Si(1)	114.20(5)
C(11)-Si(3)-Si(1)	111.97(5)
C(2)#1-C(1)-C(3)	121.46(11)
C(2)#1-C(1)-Si(1)	124.05(9)
C(3)-C(1)-Si(1)	114.42(9)
C(1)#1-C(2)-C(5)	121.20(11)
C(1)#1-C(2)-Si(1)	122.87(9)
C(5)-C(2)-Si(1)	115.65(9)
C(1)-C(3)-C(4)	110.42(10)
C(2)-C(5)-C(6)	112.10(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,-z+1

Table S5. Anisotropic displacement parameters (Å^2 x 10^3) for **1c**.

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^{2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Si(1)	13(1)	14(1)	12(1)	0(1)	2(1)	0(1)
Si(2)	18(1)	17(1)	18(1)	-1(1)	1(1)	-2(1)
Si(3)	22(1)	18(1)	18(1)	5(1)	0(1)	-1(1)
C(1)	14(1)	14(1)	18(1)	-2(1)	4(1)	-1(1)
C(2)	15(1)	16(1)	16(1)	-2(1)	5(1)	-1(1)
C(3)	16(1)	20(1)	21(1)	-2(1)	4(1)	3(1)
C(4)	24(1)	19(1)	33(1)	-4(1)	6(1)	4(1)
C(5)	22(1)	25(1)	16(1)	-2(1)	6(1)	2(1)
C(6)	27(1)	36(1)	26(1)	2(1)	14(1)	-1(1)
C(7)	52(1)	33(1)	32(1)	9(1)	-2(1)	-21(1)
C(8)	39(1)	26(1)	36(1)	-13(1)	10(1)	-5(1)
C(9)	19(1)	34(1)	51(1)	-13(1)	-3(1)	-2(1)
C(10)	42(1)	33(1)	17(1)	7(1)	3(1)	-2(1)
C(11)	26(1)	26(1)	32(1)	10(1)	-2(1)	4(1)
C(12)	30(1)	22(1)	39(1)	5(1)	6(1)	-5(1)

Table S12. Torsion angles [deg] for **1c**.

C(2)-Si(1)-Si(2)-C(7)	71.60(8)
C(1)-Si(1)-Si(2)-C(7)	-45.02(8)
Si(3)-Si(1)-Si(2)-C(7)	-167.29(7)
C(2)-Si(1)-Si(2)-C(9)	-167.95(7)
C(1)-Si(1)-Si(2)-C(9)	75.43(8)
Si(3)-Si(1)-Si(2)-C(9)	-46.84(7)
C(2)-Si(1)-Si(2)-C(8)	-45.82(7)

C(1)-Si(1)-Si(2)-C(8)	-162.43(7)
Si(3)-Si(1)-Si(2)-C(8)	75.30(6)
C(2)-Si(1)-Si(3)-C(10)	60.43(7)
C(1)-Si(1)-Si(3)-C(10)	-170.00(7)
Si(2)-Si(1)-Si(3)-C(10)	-53.90(6)
C(2)-Si(1)-Si(3)-C(12)	-60.96(7)
C(1)-Si(1)-Si(3)-C(12)	68.60(7)
Si(2)-Si(1)-Si(3)-C(12)	-175.30(6)
C(2)-Si(1)-Si(3)-C(11)	177.08(7)
C(1)-Si(1)-Si(3)-C(11)	-53.36(7)
Si(2)-Si(1)-Si(3)-C(11)	62.75(6)
C(2)-Si(1)-C(1)-C(2)#1	-13.26(14)
Si(2)-Si(1)-C(1)-C(2)#1	97.08(10)
Si(3)-Si(1)-C(1)-C(2)#1	-143.82(10)
C(2)-Si(1)-C(1)-C(3)	169.79(8)
Si(2)-Si(1)-C(1)-C(3)	-79.87(9)
Si(3)-Si(1)-C(1)-C(3)	39.22(9)
C(1)-Si(1)-C(2)-C(1)#1	13.08(14)
Si(2)-Si(1)-C(2)-C(1)#1	-98.05(10)
Si(3)-Si(1)-C(2)-C(1)#1	143.84(9)
C(1)-Si(1)-C(2)-C(5)	-172.83(8)
Si(2)-Si(1)-C(2)-C(5)	76.05(9)
Si(3)-Si(1)-C(2)-C(5)	-42.06(10)
C(2)#1-C(1)-C(3)-C(4)	84.84(15)
Si(1)-C(1)-C(3)-C(4)	-98.11(11)
C(1)#1-C(2)-C(5)-C(6)	-86.01(15)
Si(1)-C(2)-C(5)-C(6)	99.79(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,-z+1

Photoelectron spectroscopy: For compound **1b** the first band with a peak maximum at 8.5 eV represents ionization from three different orbitals that are close in energy according to the computations. The two lowest of these have b_1 and b_3 symmetries, in line with the qualitative MO-diagram (Figure 6, Main article). The splitting is rather small (70 meV) and the $2b_1$ MO is found above the $1b_3$ MO. It can also be noted that the first ionization energy of **1b** is similar to those earlier reported for 2,3-dimethyl-2-butene and **6** (8.4 and 8.8 eV, respectively).[19,20] The third orbital expected to give rise to appreciable intensity in this band is a b_1 symmetric σ-type orbital composed of in-plane p and s atomic orbitals located on both the C and Si atoms of the ring, and it is slightly shifted to higher binding energy compared to the π-type orbitals. It can also tentatively be connected to the formation of the shoulder on the high binding energy side of the band. An angle resolved study could presumably confirm the assignment since the beta value distribution of σ-orbitals is normally rather different from that of π-orbitals. The band at 9.4 eV, assigned to feature 3 in the spectrum, is connected to one single σ-orbital with b_3 symmetry.

The third band with a peak maximum at 10.3 eV is connected to ionization from four different orbitals, pair-wise similar of π-and σ-symmetry, respectively. The former two can be characterized essentially as in-phase (b_1) and out-of-phase (b_2) combinations of the two π($SiMe_2$) group orbitals. The b_1 symmetric MO also has some contribution from π(C=C), and the calculated energy separation between the two resulting MOs is 0.34 eV.

Table S6. Experimental (peak maximum from the photoelectron spectrum) and calculated binding energies (eV),[a] with assignments (term) of the **1b-II** molecule with D_2 symmetry.

Structure number	Binding energy (exp)	Binding energy (calc)	Assignment (orbital type)	Comment
1	7.9			Onset
1	8.5	8.20	b_1 (π)	Peak max
		8.27	b_3 (π)	Peak max
2	8.9	8.38	b_1 (σ)	Shoulder
3	9.4	9.24	b_3 (σ)	Peak max
4	10.3	10.11	a (σ)	Peak max
		10.26	b_2 (π)	
		10.32	b_2 (σ)	
5	10.7	10.60	b_1 (π)	Shoulder
6	11.5	11.96	b_3	Shoulder
7	12.8	11.99	b_3	Peak max
		12.01	b_2	
		12.05	a	
		12.34	b_2	
		12.38	a	
		12.43	b_3	
		12.49	a	
		12.56	b_2	
		12.62	b_1	
		12.75	b_3	
		13.26	b_1	
		13.26	b_2	
		13.30	b_3	
		13.34	a	
		13.39	b_1	
		13.62	b_2	
		13.76	b_1	
		13.80	b_3	
		13.81	a	
8	14.3	14.34	a	Peak max
		14.39	b_3	
		14.37	b_2	

[a] Calculated at ROVGF/6-311+G(d)//B3LYP/6-31G(d) level.

Table S7. Experimental (peak maximum from the photoelectron spectrum) and calculated binding energies (eV) with assignments (term) of the **1c** molecule with D_2 symmetry.

Structure number	Binding energy (exp)	Binding energy (OVGF)	Assignment (orbital type)	Comment
1	6.7			Onset
	7.1	6.76	b_1 (π)	Peak max
2	7.6			Onset
	8.3	8.02	b_3 (π)	
		8.18	b_2 (π)	
		8.28	b_1 (σ)	
		8.43	b_3 (σ)	
3	9.3	9.03	a (σ)	
		9.52	b_1 (π)	
		9.98	b_2 (σ)	
4	10.1	10.01	b_2	Peak max
		10.06	a	
		10.06	b_3	
		10.14	b_3	
		10.15	b_1	
		10.26	a	
		10.28	b_2	

[a] Calculated at ROVGF/6-311+G(d)//B3LYP/6-31G(d) level.

Table 8. Calculated[a] binding energies for **1b** and **1c** (*C*i symmetric) as well as for **1g** (D_2), **7** (C_2), **8** (C_1) and **9** (C_2).

1b-I	**1c-I**	**1g**	**7**	**8**	**9**
8.25	6.81	7.14	7.76	7.53	7.77
8.26	8.04	8.38	8.95	9.18	8.45
8.43	8.18	8.83	9.34	9.35	8.79
9.26	8.41	8.99	9.44	9.62	8.89
10.15	8.42	9.18	10.21	9.70	8.89
10.29	9.06	9.27	10.24	10.24	9.79
10.33	9.49	10.11	10.35	10.26	10.16
10.62	10.01	10.13	10.37	10.32	10.22
12.03	10.03	10.22	11.54	10.38	10.27
12.03	10.06	10.24	11.72	12.22	10.30
12.05	10.09	10.24	12.26	12.98	10.35
12.07	10.13				
12.35	10.19				
12.41	10.21				
12.47	10.29				
12.49	10.32				
12.56	11.61				
12.60	11.67				
12.84	11.93				
13.15	12.03				
13.27	12.07				
13.30					
13.34					
13.38					
13.67					
13.83					
13.84					
13.85					
14.36					
14.37					
14.41					
14.70					

[a] Calculated at ROVGF/6-311+G(d)//B3LYP/6-31G(d) level.

UV absorption spectroscopy: The first calculated transition of **1a-II**, which is dark and of B_3 symmetry, appears at 262 nm (4.74 eV) and involves excitations from HOMO-1 and HOMO-2 to LUMO (see Supplementary information). The second calculated transition, which also is dark but of B_1 symmetry, is calculated at 253 nm (4.89 eV) and it is the transition that most clearly corresponds to an excitation from HOMO to LUMO. The first transition with a significant calculated oscillator strength is of B_3 symmetry and it is found at 231 nm (5.37 eV), likely corresponding to the shoulder at ~220 nm in the experimental spectrum. The strongest allowed transition (B_3 symmetry) is found at 198 nm and calculated at 203 nm (6.09 eV). This transition has a substantial contribution of HOMO to LUMO+1 excitation. In particular, it is noteworthy that all allowed transitions of **1a-II** are of B_3 symmetry.

The first calculated transition of **1b-II** found at 240 nm is of B_3 symmetry and weakly allowed. Indeed, a longer tail towards longer wavelengths is observed in the experimental spectrum of **1b** than in that of **1a**. The first strong transition according to the calculations is the fourth transition (B_3 symmetric) with a λ_{max} of 226 nm (5.48 eV), which together with the weakly allowed fifth transitions at 220 nm (5.64 eV, B_1 symmetric), and the sixth transition at 212 nm (5.84 eV, B_3 symmetric) should represent the shoulder in the UV absorption spectrum at ~215 nm. This shoulder occurs at a similar position as for **1a**. Yet, the most visible transition in the experimental spectrum occurs at 196 nm (6.33 eV) and is of B_3 symmetry according to the computations. This transition is, however, difficult to interpret in terms of excited configurations.

For 1c, in the wavelength range 230 – 240 nm there is a clear, yet slightly weaker transition which should correspond to the B_3 symmetric transition calculated at 229 nm (5.41 eV). According to TD-DFT this state has no simple description in terms of excited configurations. The last calculated strong visible transition above 200 nm (6.21 eV) is found at 214 nm and the calculations give a B_3 symmetric transition at 222 nm (5.58 eV). The experiments reveal a strong transition at 196 nm (6.33 eV), but this excitation was not calculated as it is less than 1 eV from the first ionization energy of **1c** making the computed excitation dubious.

Table S9. Gas phase UV spectral data compared with calculated[a] values of 1a.

Exp [nm]	ε [dm^{-3}mol^{-1} cm^{-1}]	Calc. [nm (eV)]	Sym. (D_2)	f
-	-	262 (4.72)	B_3	0.002
-	-	253 (4.89)	B_1	0.007
(220)	-	231 (5.36)	B_3	0.115
-	-	225 (5.51)	B_1	0.025
-	-	208 (5.95)	A	0.000
-	-	205 (6.05)	B_1	0.001
198	14500	203 (6.09)	B_3	0.485
-	-	202 (6.11)	B_1	0.018
-	-	199 (6.22)	A	0.000
-	-	198 (6.25)	B_2	0.040
-	-	195 (6.35)	B_3	0.091

[a] TD-PBE0/6-31+G(2d)//B3LYP/6-31G(d)

Table S10. Gas phase UV spectral data compared with calculated[a] values of 1b.

Exp [nm]	ε [dm^{-3}mol^{-1} cm^{-1}]	Calc. [nm (eV)]	Sym. (D_2)	f
-	-	240 (5.16)	B_3	0.015
-	-	232 (5.35)	B_1	0.008
-	-	227 (5.46)	B_1	0.004
-	-	226 (5.48)	B_3	0.067
-	-	220 (5.63)	B_1	0.023
(215)	-	212 (5.84)	B_3	0.326
-	-	206 (6.02)	B_1	0.011
-	-	201 (6.16)	B_1	0.026
-	-	199 (6.22)	B_3	0.091
-	-	199 (6.23)	B_2	0.002
-	-	197 (6.30)	B_1	0.002
-	-	197 (6.30)	A	0.000
196	12400	196 (6.33)	B_3	0.114

[a] TD-PBE0/6-31+G(2d)//B3LYP/6-31G(d)

Table 11. Gas phase UV spectral data compared with calculated[a] values of 1c.

Exp [nm]	ε [$dm^{-3}mol^{-1} cm^{-1}$]	Calc. [nm (eV)]	Sym.	*f*
-	-	311 (3.98)	B_1	0.000
273	16200	276 (4.49)	B_3	0.356
-	-	254 (4.87)	B_1	0.039
-	-	252 (4.92)	B_3	0.016
-	-	247 (5.03)	B_1	0.000
-	-	246 (5.03)	B_3	0.019
-	-	243 (5.10)	B_2	0.002
-	-	241 (5.13)	A	0.000
-	-	241 (5.15)	B_1	0.019
-	-	235 (5.28)	A	0.000
-	-	233 (5.33)	B_2	0.046
-	-	230 (5.39)	B_1	0.031
(237)	18100	229 (5.41)	B_3	0.138
-	-	224 (5.54)	B_2	0.002
-	-	223 (5.55)	B_3	0.001
214	25200	222 (5.58)	B_3	0.381
-	-	221 (5.62)	B_1	0.000
-	-	220 (5.63)	B_2	0.017
-	-	219 (5.65)	B_3	0.000
-	-	219 (5.66)	A	0.000
-	-	215 (5.77)	B_1	0.000
-	-	215 (5.78)	A	0.015
-	-	212 (5.86)	A	0.013
-	-	211 (5.88)	B_1	0.000
-	-	210 (5.90)	B_3	0.024
-	-	208 (5.96)	B_1	0.008
-	-	207 (5.99)	A	0.000
-	-	203 (6.10)	B_3	0.024
-	-	203 (6.10)	B_2	0.008
196	26000			

[a] TD-PBE0/6-31+G(2d)//B3LYP/6-31G(d)

[b] Calculated peaks are reported until 6.10 eV, *i.e.*, 1.00 eV below the first ionization peak at 7.10 eV according to our photoelectron spectrum of **1c**.

Table S12. Singlet excited states of 1,1,4,4-tetrachloro-2,3,4,6-tetraethyl-1,4-disilacyclohexa-2,5-diene (**1a-II**) in D_2 symmetry HOMO: -7.67 eV; LUMO: -1.83 eV

State S_n	State symmetry	E (eV)	f	Main configurations (HOMO is orbital nr. 94)
n =1	B_1	4.73	0.002	0.658 (93→95) + 0.205 (92→95)
2	B_3	4.89	0.007	0.673 (94→95)
3	B_1	5.36	0.115	0.591 (92→95) + 0.327 (94→96) – 0.180 (93→95)
4	B_3	5.51	0.002	0.627 (93→96) - 0.209 (91→95) + 0.168 (92→96)
5	A	5.95	0.000	0.664 (90→95) + 0.164 (89→95)
6	B_3	6.05	0.001	0.554 (91→95) – 0.281 (92→96) + 0.278 (93→96)
7	B_1	6.09	0.485	0.549 (94→96) + 0.233 (88→95) – 0.229 (92→95)
8	B_3	6.11	0.018	0.582 (92→96) + 0.353 (91→95)
9	A	6.22	0.000	0.680 (89→95) – 0.171 (90→95)
10	B_2	6.25	0.040	0.660 (87→95) – 0.163 (90→96) - 0.102 (85→95)
11	B_1	6.35	0.091	0.644 (88→95) – 0.165 (94→96) + 0.143 (94→97)
12	B_1	6.38	0.000	0.643 (94→97) – 0.234 (94→100) – 0.139 (88→95)
13	B_3	6.51	0.004	0.615 (86→95) – 0.309 (93→97) + 0.103 (93→100)
14	B_2	6.59	0.028	0.642 (85→95) + 0.183 (90→96) + 0.171 (87→95)
15	B_3	6.59	0.003	0.584 (93→97) + 0.316 (86→95)– 0.144 (93→100)

Table S13. Comparison between the singlet excited states of 1,1,4,4-tetrachloro-2,3,4,6-tetraethyl-1,4-disilacyclohexa-2,5-diene **1a-I** and **1a-II**.

1a-I				**1a-II**			
State S_n	State symmetry	E (eV)	f	State S_n	State symmetry	E (eV)	f
n =1	AG	4.65	0.000	n =1	B_1	4.73	0.002
2	AG	4.95	0.000	2	B_3	4.89	0.007
3	AU	5.33	0.113	3	B_1	5.36	0.115
4	AU	5.52	0.026	4	B_3	5.51	0.002
5	AU	5.91	0.002	5	A	5.95	0.000
6	AU	6.05	0.049	6	B_3	6.05	0.001
7	AG	6.09	0.000	7	B_1	6.09	0.485
8	AU	6.14	0.403	8	B_3	6.11	0.018
9	AG	6.19	0.000	9	A	6.22	0.000
10	AG	6.34	0.000	10	B_2	6.25	0.040

Table S14. Singlet excited states of 2,3,4,6-tetraethyl-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (**1b-II**) in D_2 symmetry HOMO: -6.70 eV; LUMO: -0.67 eV

State S_n	State Symmetry	*E* (eV)	*f*	Main configurations (HOMO is orbital nr. 78)
n =1	B_1	5.16	0.015	0.521 (76→79) – 0.420 (78→79) - 0.131 (75→80)
2	B_2	5.35	0.008	0.475 (78→80) – 0.399 (76→80) + 0.169 (76→81) + 0.146 (75→79) – 0.142 (78→81)
3	B_2	5.46	0.004	0.625 (77→79) + 0.250 (78→80) + 0.108 (76→80)
4	B_1	5.48	0.067	0.447 (78→79) + 0.386 (77→80) + 0.348 (76→79) – 0.129 (77→81)
5	B_2	5.63	0.023	0.448 (76→80) + 0.409 (78→80) – 0.226 (77→79) – 0.152 (77→81) – 0.103 (75→79)
6	B_1	5.84	0.326	0.537 (77→80) – 0.236 (78→79) + 0.216 (77→81) - 0.206 (76→79) – 0.136 (78→84)
7	B_2	6.02	0.011	0.654 (78→81) - 0.147 (76→80) + 0.133 (78→80)
8	B_2	6.16	0.026	0.632 (75→79) + 0.226 (76→80) + 0.128 (78→81) – 0.103 (76→81)
9	B_1	6.22	0.091	0.493 (77→81) + 0.409 (75→80) + 0.176 (76→79) – 0.150 (75→81)
10	B_3	6.23	0.002	0.693 (78 → 82)
11	B_2	6.30	0.002	0.644 (76→81) + 0.193 (76→80) - 0.186 (75→79)
12	A	6.30	0.000	0.635 (78→83) + 0.279 (77→82)
13	B_1	6.33	0.114	0.480 (75→80) – 0.402 (77→81) – 0.156 (75→81) – 0.135 (78→79) – 0.113 (78→84)
14	A	6.37	0.000	0.637 (77 → 82) – 0.286 (78 → 83)
15	B_3	6.50	0.002	0.685 (77 → 83) + 0.122 (78 → 86)

Table S15. Comparison between the singlet excited states of of 2,3,4,6-tetraethyl-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene **1b-I** and **1b-II**.

1b-I				**1a-II**			
State S_n	State symmetry	*E* (eV)	*f*	State S_n	State symmetry	*E* (eV)	*f*
n =1	AG	5.09	0.000	*n* =1	B_1	5.16	0.015
2	AU	5.34	0.011	2	B_2	5.35	0.008
3	AU	5.49	0.049	3	B_2	5.46	0.004
4	AG	5.53	0.000	4	B_1	5.48	0.067
5	AG	5.61	0.000	5	B_2	5.63	0.023
6	AU	5.89	0.154	6	B_1	5.84	0.326
7	AG	6.00	0.000	7	B_2	6.02	0.011
8	AU	6.12	0.115	8	B_2	6.16	0.026
9	AU	6.17	0.280	9	B_1	6.22	0.091
10	AG	6.22	0.000	10	B_3	6.23	0.002

Table S16. Singlet excited states of 2,3,4,6-Tetraethyl-1,1,4,4-*tetrakis*(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**1c-II**) in D_2 symmetry HOMO: 5.65 eV; LUMO: -0.71 eV

State S_n	State symmetry	*E* (eV)	*f*	Main configurations (HOMO is orbital nr. 142)
n =1	B_2	3.98	0.000	0.685 (142→143)
2	B_1	4.49	0.356	0.661 (142→144) + 0.134 (141→143)
3	B_2	4.87	0.039	0.630 (142→145) + 0.272 (142→149)
4	B_1	4.92	0.016	0.622 (142→147) + 0.182 (141→143) + 0.161 (142→154) + 0.112 (139→144) + 0.103 (138→143)
5	B_2	5.03	0.000	0.440 (139→143) – 0.408 (142→149) + 0.256 (142→145) + 0.133 (141→144) + 0.111 (138→144)
6	B_1	5.03	0.010	0.521 (141→143) + 0.290 (138→143) – 0.230 (142→147) + 0.215 (139→144)
7	B_3	5.10	0.002	0.696 (142 → 146)
8	A	5.13	0.000	0.690 (142→148) – 0.125 (142→150)
9	B_2	5.15	0.019	0.471 (139→143) + 0.459 (142→149) – 0.145 (142→145)
10	A	5.28	0.000	0.630 (142→150) – 0.220 (142→158) + 0.142 (142→148)
11	B_3	5.33	0.046	0.683 (140→143)
12	B_2	5.39	0.031	0.649 (141→144) - 0.187 (139→143)
13	B_1	5.41	0.138	0.432 (139→144) + 0.343 (142→154) + 0.314 (138→143) – 0.294 (141→143) – 0.105 (142→147) + 0.105 (142→151) + 0.101 (142→144)
14	B_3	5.54	0.002	0.592 (142→155) - 0.302 (142→152) – 0.123 (142→163)
15	B_1	5.55	0.001	0.470 (139→144) - 0.378 (138→143) – 0.295 (142→154) – 0.160 (142→151)

Table S17. Comparison between the singlet excited states of 2,3,4,6-Tetraethyl-1,1,4,4-*tetrakis*(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene **1c-I** and **1c-II**.

1c-I				**1c-II**			
State S_n	State symmetry	*E* (eV)	*f*	State S_n	State symmetry	*E* (eV)	*f*
n =1	AG	4.05	0.000	*n* =1	B_2	3.98	0.000
2	AU	4.48	0.319	2	B_1	4.49	0.356
3	AG	4.95	0.000	3	B_2	4.87	0.039
4	AU	4.96	0.006	4	B_1	4.92	0.016
5	AU	5.05	0.090	5	B_2	5.03	0.000
6	AG	5.06	0.000	6	B_1	5.03	0.010
7	AG	5.11	0.000	7	B_3	5.10	0.002
8	AU	5.13	0.115	8	A	5.13	0.000
9	AG	5.20	0.000	9	B_2	5.15	0.019
10	AU	5.20	0.004	10	A	5.28	0.000

Table S18. Calculated excitation energies for **1c** (D_2), **7** (C_2), **8** (C_1) and **9** (C_2) at TD-M062X/6-31+G(2d)//B3LYP/6-31G(d) level.

	1c		**7**		**8**		**9**	
State S_n	*E* (eV)	*f*	*E* (eV)	*f*	*E* (eV)	*f*	*E* (eV)	*f*
n =1	4.28	0.000	4.94	0.321	5.08	0.014	5.41	0.022
2	4.82	0.473	5.24	0.002	5.30	0.000	5.55	0.073
3	4.99	0.025	5.39	0.001	5.37	0.030	5.74	0.065
4	5.07	0.031	5.41	0.155	5.56	0.029	5.78	0.178
5	5.14	0.064	5.56	0.015	5.87	0.229	6.06	0.006
6	5.23	0.069	5.62	0.010	5.94	0.170	6.13	0.005
7	5.39	0.003	5.78	0.095	6.02	0.033	6.28	0.123
8	5.43	0.000	5.82	0.001	6.04	0.000	6.39	0.026
9	5.45	0.000	5.90	0.003	6.18	0.000	6.43	0.038
10	5.51	0.000	5.99	0.001	6.22	0.078	6.57	0.056

Frontier orbitals and orbital energy variations in compounds 11 - 14

The energies of HOMO in dependence of C=C-C-C dihedral angle ω calculated with B3LYP/6-31G(d) closely follow the calculated first electron binding energies reported in the main text. From Figure S9 the resemblance between **11** and **12** is apparent. In comparison the energies of the HOMOs of **13** and **14** do not follow the same trend and vary only little with the dihedral angle ω. The shape of HOMO of **12** at all conformations has a strong resemblance with the HOMO of **11** (Figures S11 and S12), with the lobes on the $Si(SiMe_3)_2$ and central $C=CH_2$ fragments remaning at the ω = 90° conformation. In **13** and **14** the contribution from the central SiR_2 moieties is smaller and it vanishes at the ω = 90° conformations.

For the unoccupied orbitals and using cross-conjugated **11** as comparison, equivalent orbitals on **12** – **14** varies between being LUMO or LUMO+1. This is because there is d-orbital interaction from the Si atom which brings this orbital to lower energies. The best analogy between **11** and **12** is found at 180° where the order of the three different orbitals of **12** perfectly matches the orbital order in **11**. For **13** and **14** the contribibtion of lobes on the central SiR_2 segment to the a-symmetric unoccupied orbital (LUMO for **13** and **14**, and LUMO+1 for **12**) is much smaller than for **12**.

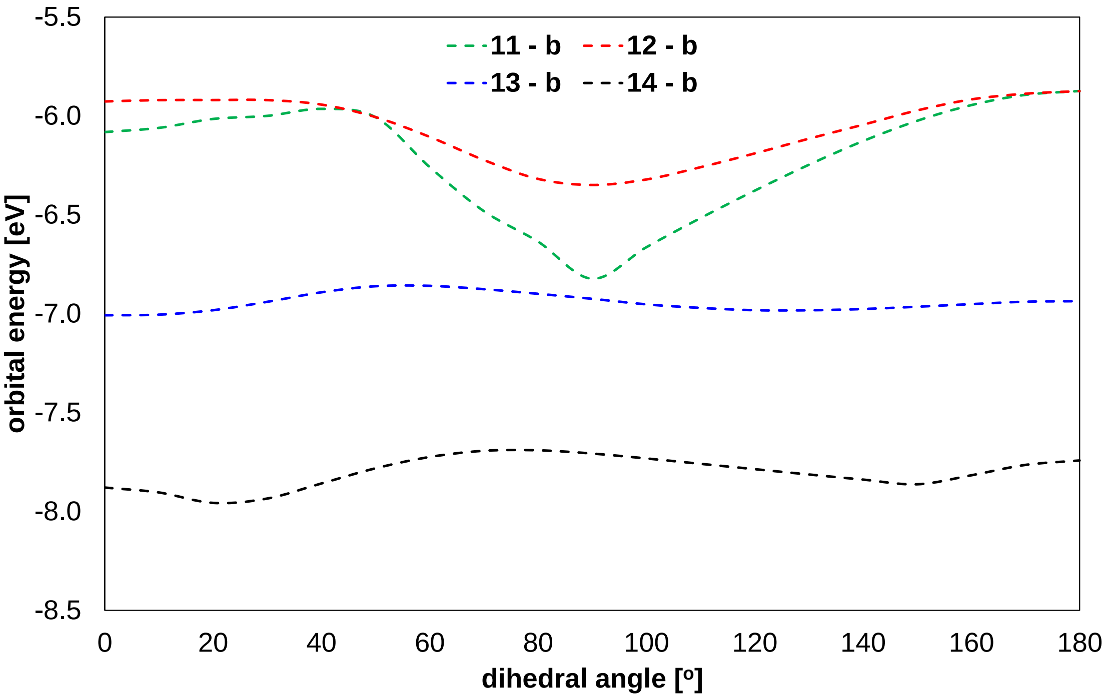


Figure S9. The energies of HOMO (all b-symmetric) of model compounds **11** – **14** as a function of C=C-C-C dihedral angle ω. Results from calculations at B3LYP/6-31G(d) level.

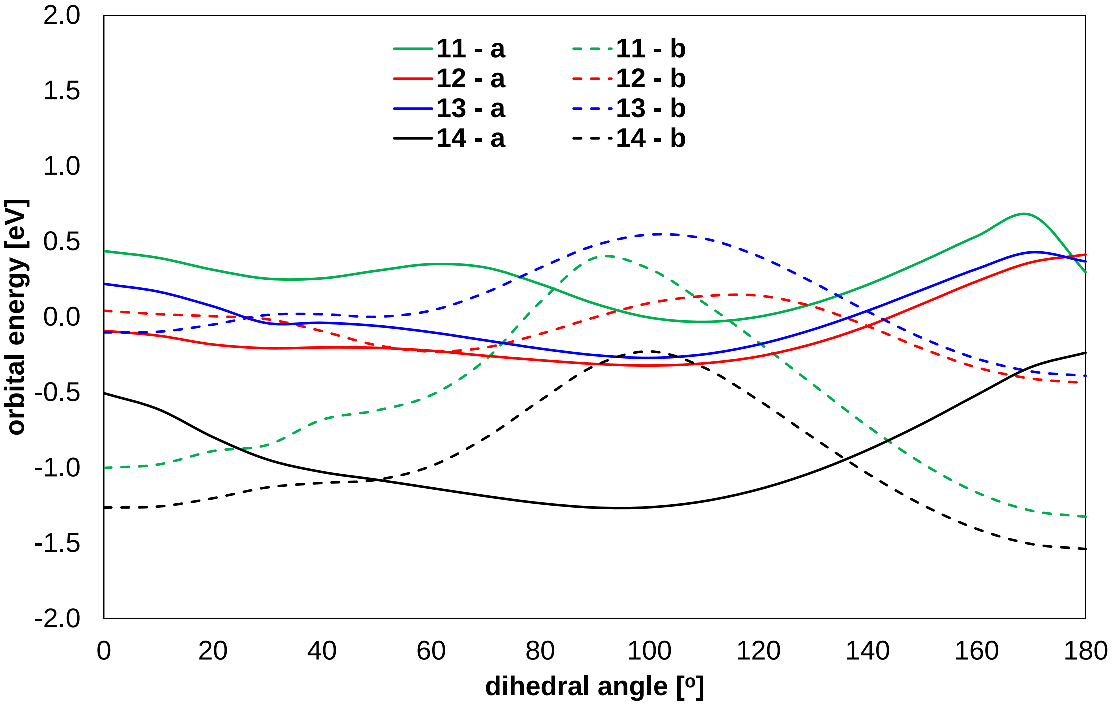


Figure S10. The energies of LUMO and LUMO+1 of model compounds **11** – **14**, a-symmetric orbitals plotted with solid lines, b-symmetric with dashed lines, as a function of the C=C-C-C dihedral angle ω. Results from calculations at B3LYP/6-31G(d) level.

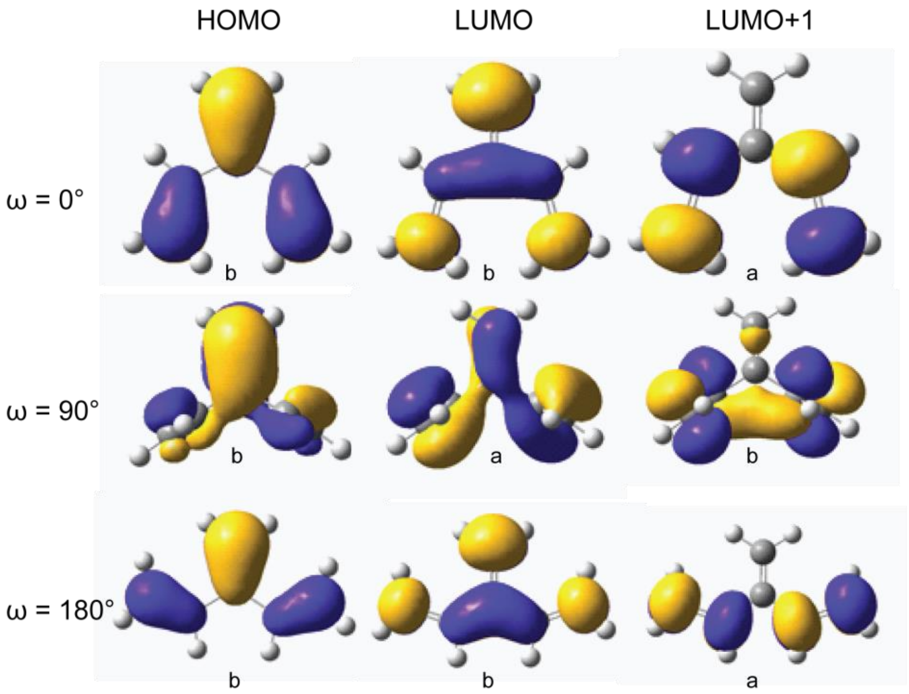


Figure S11. From left to right the HOMO, LUMO and LUMO+1 of **11** at C=C-C-C dihedral angle ω = 0° (the top three orbitals), ω = 90° (the middle three), and ω = 180° (the bottom three). Calculated at B3LYP/6-31G(d) level.

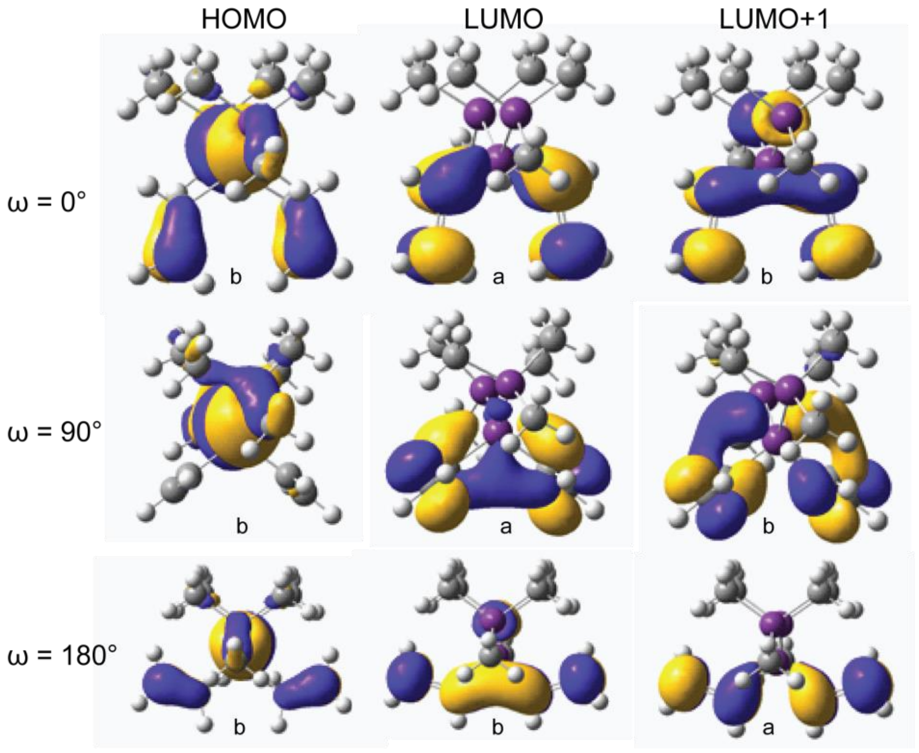


Figure S12. From left to right the HOMO, LUMO and LUMO+1 of **12** at C=C-C-C dihedral angle ω = 0° (the top three orbitals), ω = 90° (the middle three), and ω = 180° (the bottom three). Calculated at B3LYP/6-31G(d) level.

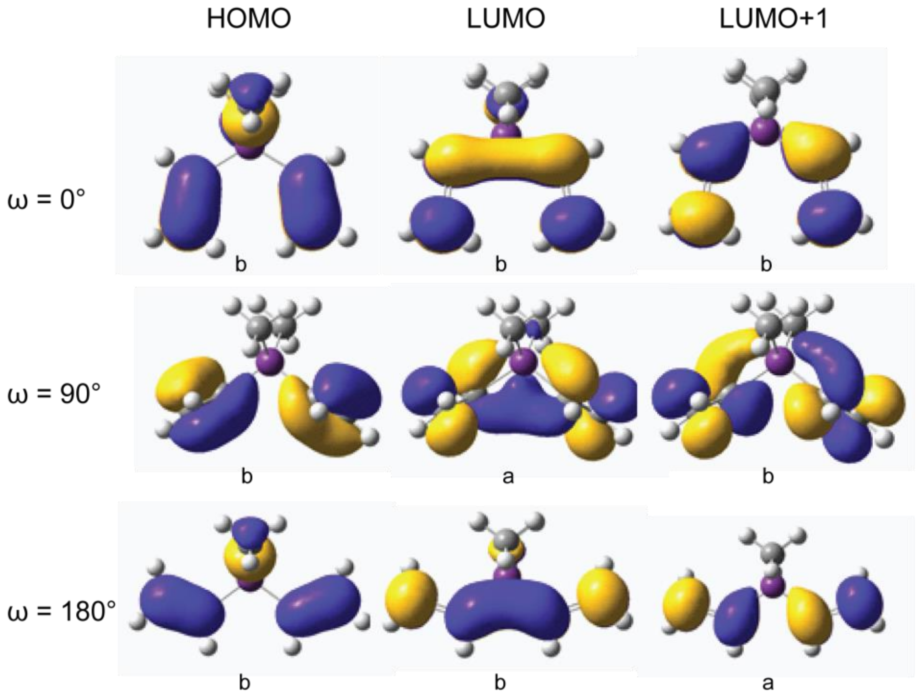


Figure S13. From left to right the HOMO, LUMO and LUMO+1 of **13** at C=C-C-C dihedral angle ω = 0° (the top three orbitals), ω = 90° (the middle three), and ω = 180° (the bottom three). Calculated at B3LYP/6-31G(d) level.

Cartesian coordinates and absolute energies

1a-I: 1,1,4,4-Tetrachloro-2,3,5,6-tetraethyl-1,4-disilacyclohex-2,5-diene (ethyl groups with up-(Si)-up-down-(Si)-down conformation)

B3LYP/6-31G(d): -2889.31632 a.u.

Point group: C_i

Cartesian coordinates:

Si	1.589385	-0.414812	0.149209
Cl	2.616511	-1.559864	1.565742
Cl	3.045903	0.203724	-1.220640
C	0.383065	-1.506496	-0.774224
C	0.905808	1.122203	0.968071
C	0.945289	-2.814170	-1.329743
H	0.513898	-3.011987	-2.316491
H	2.025705	-2.716042	-1.489294
C	0.689137	-4.022910	-0.407120
H	1.104459	-4.932278	-0.855623
H	-0.381828	-4.182636	-0.244366
H	1.158513	-3.882291	0.570328
C	1.889248	1.931130	1.812490
H	1.706574	3.001132	1.669526
H	2.913475	1.752923	1.463702
C	1.813003	1.595884	3.315823
H	2.529373	2.209046	3.873884
H	2.050561	0.544725	3.500501
H	0.813312	1.789474	3.718342
Si	-1.589385	0.414812	-0.149209
Cl	-2.616511	1.559864	-1.565742
Cl	-3.045903	-0.203724	1.220640
C	-0.383065	1.506496	0.774224
C	-0.905808	-1.122203	-0.968071
C	-0.945289	2.814170	1.329743
H	-0.513898	3.011987	2.316491
H	-2.025705	2.716042	1.489294
C	-0.689137	4.022910	0.407120
H	-1.104459	4.932278	0.855623
H	0.381828	4.182636	0.244366
H	-1.158513	3.882291	-0.570328
C	-1.889248	-1.931130	-1.812490
H	-1.706574	-3.001132	-1.669526
H	-2.913475	-1.752923	-1.463702
C	-1.813003	-1.595884	-3.315823
H	-2.529373	-2.209046	-3.873884
H	-2.050561	-0.544725	-3.500501
H	-0.813312	-1.789474	-3.718342

MP2/6-31G(d): -2884.29247 a.u.

Point group: C_i

Cartesian coordinates:

Si	1.597791	-0.395932	0.116750
Cl	2.658626	-1.517440	1.490238
Cl	2.974976	0.255956	-1.281551
C	0.389675	-1.495382	-0.776618
C	0.910706	1.117923	0.954970
C	0.939199	-2.802144	-1.323182
H	0.499032	-3.010757	-2.302980
H	2.019368	-2.712504	-1.488355
C	0.671146	-3.973413	-0.368174
H	1.068243	-4.903369	-0.786319
H	-0.400640	-4.103497	-0.197462
H	1.149283	-3.801746	0.597920
C	1.880719	1.920155	1.805764
H	1.695585	2.990399	1.673186
H	2.908160	1.745221	1.465402
C	1.772235	1.549641	3.291261
H	2.473454	2.145120	3.883753
H	2.005758	0.494472	3.444580
H	0.762647	1.731569	3.668648
Si	-1.597791	0.395932	-0.116750
Cl	-2.658626	1.517440	-1.490238
Cl	-2.974976	-0.255956	1.281551
C	-0.389675	1.495382	0.776618
C	-0.910706	-1.117923	-0.954970
C	-0.939199	2.802144	1.323182
H	-0.499032	3.010757	2.302980
H	-2.019368	2.712504	1.488355
C	-0.671146	3.973413	0.368174
H	-1.068243	4.903369	0.786319
H	0.400640	4.103497	0.197462
H	-1.149283	3.801746	-0.597920
C	-1.880719	-1.920155	-1.805764
H	-1.695585	-2.990399	-1.673186
H	-2.908160	-1.745221	-1.465402
C	-1.772235	-1.549641	-3.291261
H	-2.473454	-2.145120	-3.883753
H	-2.005758	-0.494472	-3.444580
H	-0.762647	-1.731569	-3.668648

1a-II: 1,1,4,4-Tetrachloro-2,3,5,6-tetraethyl-1,4-disilacyclohex-2,5-diene (ethyl groups with up-(Si)-down-up-(Si)-down conformation)

B3LYP/6-31G(d): -2889.31659 a.u.

Point group: D_2

Cartesian coordinates:

C	1.597186	-0.677563	-0.050845
C	1.597186	0.677563	0.050845
Si	0.000000	1.650308	0.000000
Si	0.000000	-1.650308	0.000000
C	-1.597186	0.677663	-0.050845
C	-1.597186	-0.677563	0.0508453
C	-2.883502	-1.495264	0.156943
H	-2.720372	-2.501003	-0.247704
H	-3.661767	-1.044867	-0.467817
C	-2.883501	1.495265	-0.156943
H	-3.661767	1.044867	0.467817
H	-2.720372	2.501003	0.247704
C	2.883501	1.495265	0.156943
H	2.720372	2.501003	-0.247704
H	3.661767	1.044867	-0.467817
C	2.883502	-1.495265	-0.156943
H	2.720372	-2.501003	0.247704
C	-3.397186	1.619984	-1.605521
H	-4.320675	2.209308	-1.627395
H	-3.610028	0.637551	-2.039910
H	-2.662746	2.116602	-2.245777
C	-3.397186	-1.619984	1.605521
H	-4.320675	-2.209308	1.627395
H	-3.610028	-0.637551	2.039910
H	-2.662746	-2.116602	2.245777
C	3.397185	1.619984	1.605521
H	3.610028	0.637551	2.039910
H	2.662746	2.116602	2.245777
H	4.320676	2.209308	1.627395
H	3.661767	-1.044867	0.467817
C	3.397186	-1.619984	-1.605521
H	3.610028	-0.637551	-2.039910
H	2.662746	-2.116602	-2.245777
H	4.320676	-2.209308	-1.627395
Cl	0.110596	-2.917726	1.661143
Cl	-0.110596	-2.917726	-1.661143
Cl	0.110596	2.917726	-1.661143
Cl	-0.110596	2.917726	1.661143

MP2/6-31G(d): -2884.29256 a.u.

Point group: D_2

Cartesian coordinates:

C	-0.056861	1.587444	-0.680547
C	0.056861	1.587444	0.680547
Si	0.000000	0.000000	1.651505
Si	0.000000	0.000000	-1.651505
C	-0.056861	-1.587444	0.680547
C	0.056861	-1.587444	-0.680547
C	0.194141	-2.869569	-1.483900
H	-0.179428	-2.714045	-2.502515
H	-0.432998	-3.653147	-1.047857
C	-0.194141	-2.869569	1.483900
H	0.432998	-3.653147	1.047857
H	0.179428	-2.714045	2.502515
C	0.194141	2.869569	1.483900
H	-0.179428	2.714045	2.502515
H	-0.432998	3.653147	1.047857
C	-0.194141	2.869569	-1.483900
H	0.179428	2.714045	-2.502515
C	-1.653722	-3.339973	1.548178
H	-1.729575	-4.266559	2.125254
H	-2.050854	-3.525045	0.546706
H	-2.281939	-2.586466	2.027122
C	1.653722	-3.339973	-1.548178
H	1.729575	-4.266559	-2.125254
H	2.050854	-3.525045	-0.546706
H	2.281939	-2.586466	-2.027122
C	1.653722	3.339973	1.548178
H	2.050854	3.525045	0.546706
H	2.281939	2.586466	2.027122
H	1.729575	4.266559	2.125254
H	0.432998	3.653147	-1.047857
C	-1.653722	3.339973	-1.548178
H	-2.050854	3.525045	-0.546706
H	-2.281939	2.586466	-2.027122
H	-1.729575	4.266559	-2.125254
Cl	1.650493	0.118604	-2.890921
Cl	-1.650493	-0.118604	-2.890921
Cl	-1.650493	0.118604	2.890921
Cl	1.650493	-0.118604	2.890921

1b-I: 2,3,5,6-Tetraethyl-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (ethyl groups with up-(Si)-up-down-(Si)-down conformation)
B3LYP/6-31G(d): -1208.00736 a.u.
Point group: C_i
Cartesian coordinates:

Si	0.008653	-1.670667	0.399300
C	1.583258	-0.657993	0.125542
C	-1.575275	-0.682032	0.094183
C	2.888231	-1.454072	0.229849
H	3.667833	-0.863023	0.723886
H	2.742268	-2.336044	0.867846
C	3.413658	-1.929215	-1.139039
H	4.338129	-2.507536	-1.022156
H	3.625382	-1.080058	-1.797592
H	2.681632	-2.563763	-1.648655
C	-2.869782	-1.497891	0.172660
H	-3.667450	-0.919589	0.652772
H	-2.722338	-2.378576	0.812041
C	-3.361929	-1.978569	-1.206596
H	-4.279189	-2.571608	-1.108119
H	-2.610487	-2.600454	-1.703384
H	-3.574609	-1.131637	-1.867706
Si	-0.008653	1.670667	-0.399300
C	-1.583258	0.657993	-0.125542
C	1.575275	0.682032	-0.094183
C	-2.888231	1.454072	-0.229849
H	-3.667833	0.863023	-0.723886
H	-2.742268	2.336044	-0.867846
C	-3.413658	1.929215	1.139039
H	-4.338129	2.507536	1.022156
H	-3.625382	1.080058	1.797592
H	-2.681632	2.563763	1.648655
C	2.869782	1.497891	-0.172660
H	3.667450	0.919589	-0.652772
H	2.722338	2.378576	-0.812041
C	3.361929	1.978569	1.206596
H	4.279189	2.571608	1.108119
H	2.610487	2.600454	1.703384
H	3.574609	1.131637	1.867706
C	-0.031755	3.235871	0.679293
H	-0.040839	2.995627	1.748574
H	-0.916253	3.848627	0.467655
H	0.847197	3.862468	0.485762
C	-0.005146	-2.240683	2.215847
H	0.879487	-2.843324	2.455062
H	-0.886685	-2.854236	2.438159
H	-0.017016	-1.380940	2.895343
C	0.031755	-3.235871	-0.679293
H	0.916253	-3.848627	-0.467655
H	0.040839	-2.995627	-1.748574
H	-0.847197	-3.862468	-0.485762
C	0.005146	2.240683	-2.215847
H	0.017016	1.380940	-2.895343
H	0.886685	2.854236	-2.438159
H	-0.879487	2.843324	-2.455062

MP2/6-31G(d): -1204.65010 a.u.
Point group: C_i
Cartesian coordinates:

Si	0.008406	-1.665126	0.412458
C	1.575884	-0.662026	0.125227
C	-1.567949	-0.685611	0.094041
C	2.876022	-1.450855	0.204589
H	3.661998	-0.862825	0.690229
H	2.741154	-2.341314	0.832333
C	3.350226	-1.892441	-1.185839
H	4.275078	-2.475197	-1.120004
H	3.535919	-1.024470	-1.824295
H	2.593220	-2.508971	-1.676561
C	-2.857439	-1.493848	0.147743
H	-3.661561	-0.917776	0.617758
H	-2.721675	-2.382354	0.778056
C	-3.297465	-1.942098	-1.251763
H	-4.214609	-2.538649	-1.204174
H	-2.521788	-2.547091	-1.727450
H	-3.483506	-1.076828	-1.893773
Si	-0.008406	1.665126	-0.412458
C	-1.575884	0.662026	-0.125227
C	1.567949	0.685611	-0.094041
C	-2.876022	1.450855	-0.204589
H	-3.661998	0.862825	-0.690229
H	-2.741154	2.341314	-0.832333
C	-3.350226	1.892441	1.185839
H	-4.275078	2.475197	1.120004
H	-3.535919	1.024470	1.824295
H	-2.593220	2.508971	1.676561
C	2.857439	1.493848	-0.147743
H	3.661561	0.917776	-0.617758
H	2.721675	2.382354	-0.778056
C	3.297465	1.942098	1.251763
H	4.214609	2.538649	1.204174
H	2.521788	2.547091	1.727450
H	3.483506	1.076828	1.893773
C	-0.030626	3.243555	0.632837
H	-0.039557	3.020510	1.704000
H	-0.914086	3.849734	0.406681
H	0.847919	3.862987	0.424124
C	-0.005733	-2.185609	2.234105

H	0.878620	-2.779139	2.488634
H	-0.886404	-2.791637	2.471357
H	-0.018324	-1.304434	2.882771
C	0.030626	-3.243555	-0.632837
H	0.914086	-3.849734	-0.406681
H	0.039557	-3.020510	-1.704000
H	-0.847919	-3.862987	-0.424124
C	0.005733	2.185609	-2.234105
H	0.018324	1.304434	-2.882771
H	0.886404	2.791637	-2.471357
H	-0.878620	2.779139	-2.488634

1b-II: 2,3,5,6-Tetraethyl-1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene (ethyl groups with up-(Si)-down-up-(Si)-down conformation)
B3LYP/6-31G(d): -1208.00692 a.u.
Point group: D_2
Cartesian coordinates:

C	0.676962	-1.578359	0.053148
C	-0.676962	-1.578359	-0.053148
Si	-1.718665	0.000000	0.000000
Si	1.718665	0.000000	0.000000
C	-0.676962	1.578359	0.053148
C	0.676962	1.578359	-0.053148
C	2.848110	-0.093192	-1.528964
H	2.264326	-0.127632	-2.455919
H	3.483761	-0.986435	-1.502819
H	3.514531	0.775932	-1.584236
C	2.848110	0.093192	1.528964
H	3.483761	0.986435	1.502819
H	3.514531	-0.775932	1.584236
H	2.264326	0.127632	2.455919
C	1.478862	2.878953	-0.172460
H	2.492223	2.737506	0.225810
H	1.032335	3.670464	0.440116
C	-1.478862	2.878953	0.172460
H	-1.032335	3.670464	-0.440116
H	-2.492223	2.7375058	-0.225810
C	-2.848110	-0.093192	1.528964
H	-3.514531	0.775932	1.584236
H	-2.264326	-0.127632	2.455919
H	-3.483761	-0.986435	1.502819
C	-2.848110	0.093192	-1.528964
H	-2.264326	0.127632	-2.455920
H	-3.483761	0.986435	-1.502819
H	-3.514531	-0.775932	-1.584236
C	-1.478862	-2.878953	-0.172460
H	-2.492223	-2.737506	0.225810
H	-1.032335	-3.670464	0.440116
C	1.478862	-2.878953	0.172460
H	2.492223	-2.737506	-0.225810
C	-1.596158	3.378189	1.626062
H	-2.186792	4.301038	1.674402
H	-0.609308	3.583870	2.054476
H	-2.081713	2.633816	2.265439
C	1.596158	3.378189	-1.626062
H	2.186792	4.301038	-1.674402
H	0.609308	3.583870	-2.054476
H	2.081713	2.633816	-2.265439
C	-1.596158	-3.378189	-1.626062
H	-0.609308	-3.583870	-2.054476
H	-2.081713	-2.633816	-2.265439
H	-2.186792	-4.301038	-1.674402
H	1.032335	-3.670464	-0.440116
C	1.596158	-3.378189	1.626062
H	0.609308	-3.583870	2.054476
H	2.081713	-2.633816	2.265439
H	2.186792	-4.301038	1.674402

MP2/6-31G(d): -1204.64946 a.u.
Point group: D_2
Cartesian coordinates:

C	1.569901	0.056898	-0.680428
C	1.569901	-0.056898	0.680428
Si	0.000000	0.000000	1.718849
Si	0.000000	0.000000	-1.718849
C	-1.569901	0.056898	0.680428
C	-1.569901	-0.056898	-0.680428
C	0.096720	-1.525776	-2.837134
H	0.128245	-2.445641	-2.245217
H	0.990719	-1.501984	-3.468772
H	-0.769996	-1.581034	-3.504092
C	-0.096720	1.525776	-2.837134
H	-0.990719	1.501984	-3.468772
H	0.769996	1.581034	-3.504092
H	-0.128245	2.445641	-2.245217
C	-2.865818	-0.207735	-1.466478
H	-2.734239	0.161050	-2.491549
H	-3.662754	0.404650	-1.031442
C	-2.865818	0.207735	1.466478
H	-3.662754	-0.404650	1.031442
H	-2.734239	-0.161050	2.491549
C	0.096720	1.525776	2.837134
H	-0.769996	1.581034	3.504092
H	0.128245	2.445641	2.245217
H	0.990719	1.501984	3.468772
C	-0.096720	-1.525776	2.837134
H	-0.128245	-2.445641	2.245217

H	-0.990719	-1.501984	3.468772
H	0.769996	-1.581034	3.504092
C	2.865818	-0.207735	1.466478
H	2.734239	0.161050	2.491549
H	3.662754	0.404650	1.031442
C	2.865818	0.207735	-1.466478
H	2.734239	-0.161050	-2.491549
C	-3.317075	1.673046	1.523149
H	-4.238126	1.778789	2.106058
H	-3.500505	2.060902	0.517537
H	-2.548270	2.298007	1.983969
C	-3.317075	-1.673046	-1.523149
H	-4.238126	-1.778789	-2.106058
H	-3.500505	-2.060902	-0.517537
H	-2.548270	-2.298007	-1.983969
C	3.317075	-1.673046	1.523149
H	3.500505	-2.060902	0.517537
H	2.548270	-2.298007	1.983969
H	4.238126	-1.778789	2.106058
H	3.662754	-0.404650	-1.031442
C	3.317075	1.673046	-1.523149
H	3.500505	2.060902	-0.517537
H	2.548270	2.298007	-1.983969
H	4.238126	1.778789	-2.106058

1c-I: 1,1,4,4-*Tetrakis*(trimethylsilyl)-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene (ethyl groups with up-(Si)-up-down-(Si)-down conformation)
B3LYP/6-31G(d): -2685.38811 a.u.
Point group: C_i
Cartesian coordinates:

Si	-0.756808	0.368264	-1.528749
Si	-2.246289	-1.360201	-2.274035
Si	-0.714848	2.168915	-3.129465
C	-1.450138	0.906205	0.164250
C	0.936204	-0.494095	-1.354905
C	-2.716498	1.768429	0.100446
H	-3.450697	1.445611	0.846924
H	-3.209792	1.639247	-0.870433
C	-2.437264	3.270379	0.302654
H	-2.008731	3.469222	1.290351
H	-3.361481	3.854145	0.211751
H	-1.728171	3.646988	-0.440570
C	1.658749	-0.792000	-2.674200
H	0.944395	-0.786376	-3.505609
H	2.089315	-1.799559	-2.666305
C	2.778487	0.217674	-2.994303
H	2.390920	1.239246	-3.050095
H	3.249475	-0.015513	-3.957154
H	3.558646	0.207799	-2.226319
C	-2.293087	-2.705798	-0.931544
H	-2.664723	-2.304921	0.018090
H	-1.294266	-3.116636	-0.746895
H	-2.949569	-3.533214	-1.229914
C	-1.678653	-2.179799	-3.898364
H	-0.675628	-2.611950	-3.811007
H	-1.667189	-1.477262	-4.739705
H	-2.366838	-2.994357	-4.160091
C	-4.028830	-0.744578	-2.546105
H	-4.665289	-1.580510	-2.864974
H	-4.087581	0.027843	-3.321431
H	-4.464509	-0.331331	-1.629678
C	-0.167115	1.563649	-4.852927
H	-0.258238	2.393313	-5.566454
H	-0.804101	0.749254	-5.216761
H	0.869955	1.217134	-4.883415
C	-2.448676	2.911045	-3.416168
H	-2.371566	3.717461	-4.157625
H	-2.897903	3.336241	-2.513784
H	-3.145044	2.166021	-3.818075
C	0.445117	3.589187	-2.611753
H	1.469764	3.244897	-2.434644
H	0.107042	4.084881	-1.694753
H	0.480477	4.348689	-3.403856
Si	0.756808	-0.368264	1.528749
Si	2.246289	1.360201	2.274035
Si	0.714848	-2.168915	3.129465
C	1.450138	-0.906205	-0.164250
C	-0.936204	0.494095	1.354905
C	2.716498	-1.768429	-0.100446
H	3.450697	-1.445611	-0.846924
H	3.209792	-1.639247	0.870433
C	2.437264	-3.270379	-0.302654
H	2.008731	-3.469222	-1.290351
H	3.361481	-3.854145	-0.211751
H	1.728171	-3.646988	0.440570
C	-1.658749	0.792000	2.674200
H	-0.944395	0.786376	3.505609
H	-2.089315	1.799559	2.666305
C	-2.778487	-0.217674	2.994303
H	-2.390920	-1.239246	3.050095
H	-3.249475	0.015513	3.957154
H	-3.558646	-0.207799	2.226319
C	2.293087	2.705798	0.931544
H	2.664723	2.304921	-0.018090
H	1.294266	3.116636	0.746895
H	2.949569	3.533214	1.229914
C	1.678653	2.179799	3.898364

H	0.675628	2.611950	3.811007
H	1.667189	1.477262	4.739705
H	2.366838	2.994357	4.160091
C	4.028830	0.744578	2.546105
H	4.665289	1.580510	2.864974
H	4.087581	-0.027843	3.321431
H	4.464509	0.331331	1.629678
C	0.167115	-1.563649	4.852927
H	0.258238	-2.393313	5.566454
H	0.804101	-0.749254	5.216761
H	-0.869955	-1.217134	4.883415
C	2.448676	-2.911045	3.416168
H	2.371566	-3.717461	4.157625
H	2.897903	-3.336241	2.513784
H	3.145044	-2.166021	3.818075
C	-0.445117	-3.589187	2.611753
H	-1.469764	-3.244897	2.434644
H	-0.107042	-4.084881	1.694753
H	-0.480477	-4.348689	3.403856

MP2/6-31G(d): -2678.72794 a.u.
Point group: C_i
Cartesian coordinates:

Si	-0.723988	0.446131	-1.505839
Si	-2.159465	-1.310335	-2.187290
Si	-0.713833	2.233242	-3.076022
C	-1.429074	0.932040	0.183776
C	0.940018	-0.447966	-1.365847
C	-2.660967	1.825827	0.150161
H	-3.396166	1.511273	0.898809
H	-3.163956	1.736124	-0.820189
C	-2.292109	3.295435	0.386440
H	-1.852695	3.430380	1.378905
H	-3.172380	3.943255	0.309914
H	-1.554940	3.633288	-0.345484
C	1.667741	-0.694853	-2.680578
H	0.955337	-0.668727	-3.512868
H	2.112611	-1.695652	-2.701437
C	2.761335	0.350429	-2.929020
H	2.345340	1.360207	-2.916580
H	3.245305	0.192129	-3.899200
H	3.530168	0.302486	-2.152582
C	-2.276256	-2.465319	-0.690952
H	-2.801537	-1.983935	0.139301
H	-1.275077	-2.732861	-0.336362
H	-2.806806	-3.390799	-0.943263
C	-1.453439	-2.305291	-3.640301
H	-0.487275	-2.749683	-3.382232
H	-1.313911	-1.691405	-4.535509
H	-2.136609	-3.122275	-3.900064
C	-3.907243	-0.746741	-2.663216
H	-4.543895	-1.617590	-2.857850
H	-3.901470	-0.133103	-3.569590
H	-4.377520	-0.164311	-1.864968
C	-0.220879	1.594492	-4.795243
H	-0.352181	2.399684	-5.527695
H	-0.853077	0.757849	-5.109945
H	0.820924	1.269204	-4.846317
C	-2.454430	2.959995	-3.295056
H	-2.436796	3.679151	-4.122517
H	-2.807226	3.489516	-2.406958
H	-3.189078	2.188568	-3.543654
C	0.443529	3.669175	-2.631286
H	1.478072	3.347243	-2.487081
H	0.129806	4.178061	-1.715434
H	0.431904	4.408717	-3.440742
Si	0.723988	-0.446131	1.505839
Si	2.159465	1.310335	2.187290
Si	0.713833	-2.233242	3.076022
C	1.429074	-0.932040	-0.183776
C	-0.940018	0.447966	1.365847
C	2.660967	-1.825827	-0.150161
H	3.396166	-1.511273	-0.898809
H	3.163956	-1.736124	0.820189
C	2.292109	-3.295435	-0.386440
H	1.852695	-3.430380	-1.378905
H	3.172380	-3.943255	-0.309914
H	1.554940	-3.633288	0.345484
C	-1.667741	0.694853	2.680578
H	-0.955337	0.668727	3.512868
H	-2.112611	1.695652	2.701437
C	-2.761335	-0.350429	2.929020
H	-2.345340	-1.360207	2.916580
H	-3.245305	-0.192129	3.899200
H	-3.530168	-0.302486	2.152582
C	2.276256	2.465319	0.690952
H	2.801537	1.983935	-0.139301
H	1.275077	2.732861	0.336362
H	2.806806	3.390799	0.943263
C	1.453439	2.305291	3.640301
H	0.487275	2.749683	3.382232
H	1.313911	1.691405	4.535509
H	2.136609	3.122275	3.900064
C	3.907243	0.746741	2.663216
H	4.543895	1.617590	2.857850
H	3.901470	0.133103	3.569590
H	4.377520	0.164311	1.864968
C	0.220879	-1.594492	4.795243
H	0.352181	-2.399684	5.527695
H	0.853077	-0.757849	5.109945

H	-0.820924	-1.269204	4.846317
C	2.454430	-2.959995	3.295056
H	2.436796	-3.679151	4.122517
H	2.807226	-3.489516	2.406958
H	3.189078	-2.188568	3.543654
C	-0.443529	-3.669175	2.631286
H	-1.478072	-3.347243	2.487081
H	-0.129806	-4.178061	1.715434
H	-0.431904	-4.408717	3.440742

M062X/6-311G(d): -641.7401772 a.u.
Point group: C_i
Cartesian coordinates:

Si	-0.71907	0.47138	-1.48278
Si	-2.15857	-1.26894	-2.16954
Si	-0.72598	2.26312	-3.02402
C	-1.41450	0.93647	0.21161
C	0.92523	-0.45178	-1.37083
C	-2.64906	1.82685	0.17294
H	-3.37947	1.52583	0.92893
H	-3.15779	1.72545	-0.79242
C	-2.26997	3.29692	0.38485
H	-1.83479	3.44726	1.37539
H	-3.13729	3.95489	0.28853
H	-1.52174	3.61562	-0.34410
C	1.62736	-0.68448	-2.70211
H	0.90138	-0.66153	-3.52119
H	2.08523	-1.67684	-2.74315
C	2.69698	0.38278	-2.95799
H	2.27195	1.38609	-2.88422
H	3.14008	0.27401	-3.95106
H	3.49862	0.31907	-2.21889
C	-2.39574	-2.30030	-0.60657
H	-2.95561	-1.75244	0.15552
H	-1.42237	-2.55401	-0.17154
H	-2.92397	-3.23548	-0.81432
C	-1.34191	-2.37111	-3.46859
H	-0.39719	-2.77765	-3.09700
H	-1.13349	-1.84339	-4.40274
H	-1.99396	-3.21699	-3.70694
C	-3.83323	-0.70537	-2.83612
H	-4.48061	-1.56733	-3.02387
H	-3.72285	-0.16815	-3.78216
H	-4.35678	-0.04742	-2.13762
C	-0.26188	1.60287	-4.73521
H	-0.43995	2.37793	-5.48718
H	-0.86858	0.73563	-5.01206
H	0.78862	1.31346	-4.80847
C	-2.47730	2.96333	-3.18898
H	-2.51270	3.64261	-4.04665
H	-2.78989	3.53164	-2.31043
H	-3.21983	2.18029	-3.36169
C	0.42413	3.70618	-2.61336
H	1.46745	3.40518	-2.50007
H	0.13417	4.21740	-1.69274
H	0.37988	4.44284	-3.42216
Si	0.71907	-0.47138	1.48278
Si	2.15857	1.26894	2.16954
Si	0.72598	-2.26312	3.02402
C	1.41450	-0.93647	-0.21161
C	-0.92523	0.45178	1.37083
C	2.64906	-1.82685	-0.17294
H	3.37947	-1.52583	-0.92893
H	3.15779	-1.72545	0.79242
C	2.26997	-3.29692	-0.38485
H	1.83479	-3.44726	-1.37539
H	3.13729	-3.95489	-0.28853
H	1.52174	-3.61562	0.34410
C	-1.62736	0.68448	2.70211
H	-0.90138	0.66153	3.52119
H	-2.08523	1.67684	2.74315
C	-2.69698	-0.38278	2.95799
H	-2.27195	-1.38609	2.88422
H	-3.14008	-0.27401	3.95106
H	-3.49862	-0.31907	2.21889
C	2.39574	2.30030	0.60657
H	2.95561	1.75244	-0.15552
H	1.42237	2.55401	0.17154
H	2.92397	3.23548	0.81432
C	1.34191	2.37111	3.46859
H	0.39719	2.77765	3.09700
H	1.13349	1.84339	4.40274
H	1.99396	3.21699	3.70694
C	3.83323	0.70537	2.83612
H	4.48061	1.56733	3.02387
H	3.72285	0.16815	3.78216
H	4.35678	0.04742	2.13762
C	0.26188	-1.60287	4.73521
H	0.43995	-2.37793	5.48718
H	0.86858	-0.73563	5.01206
H	-0.78862	-1.31346	4.80847
C	2.47730	-2.96333	3.18898
H	2.51270	-3.64261	4.04665
H	2.78989	-3.53164	2.31043
H	3.21983	-2.18029	3.36169
C	-0.42413	-3.70618	2.61336
H	-1.46745	-3.40518	2.50007
H	-0.13417	-4.21740	1.69274
H	-0.37988	-4.44284	3.42216

M062X/6-311G(d): -641.7401587 a.u.
Point group: C_1
Cartesian coordinates:

Si	-1.71022	-0.13812	0.01718
Si	-2.25891	-2.42160	0.24668
Si	-3.65108	1.20582	-0.11147
C	-0.67072	0.19073	1.56078
C	-0.67788	-0.16515	-1.56492
C	-1.46911	0.39087	2.84164
H	-0.98445	-0.09900	3.69055
H	-2.45617	-0.07643	2.74923
C	-1.64982	1.88214	3.14745
H	-0.68448	2.36227	3.32207
H	-2.27595	2.03947	4.02928
H	-2.11613	2.39938	2.30626
C	-1.48313	-0.24230	-2.85554
H	-2.46625	-0.68217	-2.65921
H	-1.00609	-0.90286	-3.58512
C	-1.67678	1.14640	-3.47335
H	-2.10615	1.83926	-2.74666
H	-2.34117	1.10926	-4.34029
H	-0.72299	1.57021	-3.79536
C	-0.66537	-3.21146	0.87985
H	-0.42228	-2.86107	1.88618
H	0.17594	-2.94123	0.23205
H	-0.73483	-4.30296	0.90319
C	-2.67711	-3.20242	-1.42183
H	-1.86123	-3.06011	-2.13585
H	-3.58489	-2.78599	-1.86619
H	-2.83182	-4.27954	-1.30605
C	-3.67276	-2.78161	1.44650
H	-3.77342	-3.85932	1.60720
H	-4.62798	-2.41915	1.05663
H	-3.51420	-2.31759	2.42385
C	-4.72047	0.58843	-1.54563
H	-5.69738	1.08078	-1.51222
H	-4.89703	-0.48924	-1.47759
H	-4.28275	0.79440	-2.52473
C	-4.70318	0.99016	1.44599
H	-5.67462	1.47005	1.28953
H	-4.25540	1.44382	2.33227
H	-4.89368	-0.06276	1.66909
C	-3.34966	3.05644	-0.34942
H	-2.74405	3.28089	-1.22966
H	-2.85061	3.51107	0.50903
H	-4.31152	3.56452	-0.47330
Si	1.71017	0.13810	-0.01718
Si	2.25898	2.42156	-0.24672
Si	3.65104	-1.20580	0.11155
C	0.67066	-0.19071	-1.56078
C	0.67783	0.16514	1.56492
C	1.46903	-0.39066	-2.84167
H	0.98428	0.09921	-3.69052
H	2.45604	0.07676	-2.74927
C	1.64989	-1.88189	-3.14758
H	0.68458	-2.36211	-3.32217
H	2.27598	-2.03910	-4.02946
H	2.11629	-2.39913	-2.30645
C	1.48308	0.24214	2.85555
H	2.46623	0.68196	2.65925
H	1.00608	0.90267	3.58518
C	1.67666	-1.14662	3.47326
H	2.10608	-1.83943	2.74655
H	2.34098	-1.10957	4.34026
H	0.72284	-1.57045	3.79516
C	0.66553	3.21150	-0.88004
H	0.42257	2.86119	-1.88643
H	-0.17588	2.94126	-0.23238
H	0.73504	4.30300	-0.90329
C	2.67712	3.20240	1.42179
H	1.86121	3.06008	2.13578
H	3.58489	2.78598	1.86619
H	2.83182	4.27952	1.30601
C	3.67290	2.78147	-1.44647
H	3.77364	3.85918	-1.60719
H	4.62809	2.41896	-1.05658
H	3.51435	2.31745	-2.42383
C	4.72034	-0.58830	1.54574
H	5.69729	-1.08058	1.51237
H	4.89682	0.48938	1.47771
H	4.28259	-0.79431	2.52481
C	4.70323	-0.99019	-1.44587
H	5.67468	-1.47002	-1.28932
H	4.25553	-1.44395	-2.33215
H	4.89369	0.06272	-1.66904
C	3.34968	-3.05643	0.34957
H	2.74387	-3.28087	1.22967
H	2.85089	-3.51114	-0.50899
H	4.31155	-3.56443	0.47371

1c-II: 1,1,4,4-*Tetrakis*(trimethylsilyl)-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene (ethyl groups with up-(Si)-down-up-(Si)-down conformation)
B3LYP/6-31G(d): -2685.38718 a.u.
Point group: D_2
Cartesian coordinates:

C	-0.671984	-0.107249	1.571401
C	0.671984	0.107249	1.571401

Si	1.743049	0.000000	0.000000
Si	-1.743049	0.000000	0.000000
C	1.444130	0.341659	2.875654
H	2.512234	0.153489	2.721947
H	1.129763	-0.362011	3.655317
C	-1.444130	-0.341659	2.875654
H	-2.512240	-0.153489	2.721947
H	-1.129763	0.362011	3.655317
Si	-3.114773	1.955600	0.255368
Si	-3.114773	-1.955600	-0.255368
Si	3.114773	-1.955600	0.255368
Si	3.114773	1.955600	-0.255368
C	4.119889	-1.937591	1.875646
H	4.754367	-1.048456	1.964323
H	4.778581	-2.815828	1.902447
H	3.478987	-1.980593	2.762803
C	4.392062	-2.130536	-1.149726
H	5.102420	-1.295065	-1.154343
H	3.933159	-2.182652	-2.142369
H	4.972944	-3.051177	-1.006039
C	4.119889	1.937591	-1.875646
H	4.778581	2.815828	-1.902447
H	3.478987	1.980593	-2.762804
H	4.754367	1.048456	-1.964323
C	-4.392062	2.130536	-1.149726
H	-4.972944	3.051177	-1.006038
H	-5.102420	1.295065	-1.154343
H	-3.933159	2.182652	-2.142369
C	-4.119889	1.937591	1.875646
H	-4.778581	2.815828	1.902447
H	-3.478987	1.980594	2.762804
H	-4.754367	1.048456	1.964323
C	-2.028087	3.517645	0.2989967
H	-2.649291	4.413148	0.430560
H	-1.443486	3.647973	-0.618131
H	-1.319749	3.477063	1.134647
C	-4.392062	-2.130536	1.149726
H	-3.933159	-2.182652	2.142369
H	-4.972944	-3.051177	1.006039
H	-5.102420	-1.295065	1.154343
C	-2.028087	-3.517645	-0.298997
H	-1.319749	-3.477063	-1.134647
H	-2.649291	-4.413148	-0.430560
H	-1.443486	-3.647973	0.618131
C	-4.119889	-1.937591	-1.875646
H	-4.754367	-1.048456	-1.964323
H	-4.778581	-2.815828	-1.902447
H	-3.478987	-1.980594	-2.762804
C	1.290624	1.777532	3.416530
H	0.247188	2.012965	3.648855
H	1.636015	2.517397	2.687691
H	1.878514	1.910189	4.333020
C	-1.290624	-1.777532	3.416530
H	-1.878514	-1.910189	4.333020
H	-0.247188	-2.012965	3.648855
H	-1.636015	-2.517397	2.687691
C	-0.671984	0.107249	-1.571401
C	0.671984	-0.107249	-1.571401
C	-1.444130	0.341659	-2.875654
H	-2.512240	0.153489	-2.721947
H	-1.129763	-0.362011	-3.655317
C	1.444130	-0.341659	-2.875654
H	1.129763	0.362011	-3.655317
H	2.512240	-0.153489	-2.721947
C	-1.290624	1.777532	-3.416530
H	-0.247188	2.012965	-3.648855
H	-1.636015	2.517397	-2.687691
H	-1.878514	1.910189	-4.333020
C	1.290624	-1.777532	-3.416530
H	1.878514	-1.910189	-4.333020
H	0.247188	-2.012965	-3.648855
H	1.636015	-2.517397	-2.687691
C	4.392062	2.130536	1.149726
H	5.1024196	1.295065	1.154343
H	3.933159	2.182652	2.142369
H	4.972943	3.051177	1.006039
C	2.028087	3.517645	-0.298997
H	1.319749	3.477063	-1.134647
H	2.649291	4.413148	-0.430560
H	1.443486	3.647973	0.618131
C	2.028087	-3.517645	0.298997
H	1.443486	-3.647973	-0.618131
H	1.319749	-3.477063	1.134647
H	2.649291	-4.413148	0.430560

MP2/6-31G(d): -2678.72541 a.u.
Point group: D_2
Cartesian coordinates:

C	-1.564219	0.119530	0.673827
C	-1.564219	-0.119530	-0.673827
Si	0.000000	0.000000	-1.732026
Si	0.000000	0.000000	1.732026
C	-2.860957	-0.390844	-1.425864
H	-2.724878	-0.210251	-2.497460
H	-3.659830	0.287218	-1.104640
C	-2.860957	0.390844	1.425864
H	-2.724878	0.210251	2.497460
H	-3.659830	-0.287218	1.104640
Si	-0.303418	-1.942442	3.058827
Si	0.303418	1.942442	3.058827

Si	-0.303418	1.942442	-3.058827
Si	0.303418	-1.942442	-3.058827
C	-1.921255	1.899667	-4.051732
H	-2.008935	1.002116	-4.671386
H	-1.958207	2.768907	-4.718979
H	-2.798046	1.947690	-3.399638
C	1.088292	2.162809	-4.330668
H	1.083546	1.343471	-5.057365
H	2.081286	2.201823	-3.875896
H	0.939474	3.095539	-4.887057
C	1.921255	-1.899667	-4.051732
H	1.958207	-2.768907	-4.718979
H	2.798046	-1.947690	-3.399638
H	2.008935	-1.002116	-4.671386
C	1.088292	-2.162809	4.330668
H	0.939474	-3.095539	4.887057
H	1.083546	-1.343471	5.057365
H	2.081286	-2.201823	3.875896
C	-1.921255	-1.899667	4.051732
H	-1.958207	-2.768907	4.718979
H	-2.798046	-1.947690	3.399638
H	-2.008935	-1.002116	4.671386
C	-0.399991	-3.461071	1.930499
H	-0.566616	-4.371151	2.518294
H	0.506878	-3.601996	1.336619
H	-1.235337	-3.355116	1.230147
C	-1.088292	2.162809	4.330668
H	-2.081286	2.201823	3.875896
H	-0.939474	3.095539	4.887057
H	-1.083546	1.343471	5.057365
C	0.399991	3.461071	1.930499
H	1.235337	3.355116	1.230147
H	0.566616	4.371151	2.518294
H	-0.506878	3.601996	1.336619
C	1.921255	1.899667	4.051732
H	2.008935	1.002116	4.671386
H	1.958207	2.768907	4.718979
H	2.798046	1.947690	3.399638
C	-3.316398	-1.842982	-1.229441
H	-3.511526	-2.053325	-0.174246
H	-2.544468	-2.539142	-1.565968
H	-4.231446	-2.048462	-1.795913
C	-3.316398	1.842982	1.229441
H	-4.231446	2.048462	1.795913
H	-3.511526	2.053325	0.174246
H	-2.544468	2.539142	1.565968
C	1.564219	-0.119530	0.673827
C	1.564219	0.119530	-0.673827
C	2.860957	-0.390844	1.425864
H	2.724878	-0.210251	2.497460
H	3.659830	0.287218	1.104640
C	2.860957	0.390844	-1.425864
H	3.659830	-0.287218	-1.104640
H	2.724878	0.210251	-2.497460
C	3.316398	-1.842982	1.229441
H	3.511526	-2.053325	0.174246
H	2.544468	-2.539142	1.565968
H	4.231446	-2.048462	1.795913
C	3.316398	1.842982	-1.229441
H	4.231446	2.048462	-1.795913
H	3.511526	2.053325	-0.174246
H	2.544468	2.539142	-1.565968
C	-1.088292	-2.162809	-4.330668
H	-1.083546	-1.343471	-5.057365
H	-2.081286	-2.201823	-3.875896
H	-0.939474	-3.095539	-4.887057
C	0.399991	-3.461071	-1.930499
H	1.235337	-3.355116	-1.230147
H	0.566616	-4.371151	-2.518294
H	-0.506878	-3.601996	-1.336619
C	-0.399991	3.461071	-1.930499
H	0.506878	3.601996	-1.336619
H	-1.235337	3.355116	-1.230147
H	-0.566616	4.371151	-2.518294
H	1.464143	4.262179	-2.463919
C	-2.381482	4.340144	-0.655224
H	-1.733022	5.076872	-0.169692
H	-3.417704	4.653439	-0.480385
H	-2.201594	4.389889	-1.731964
C	3.428291	2.838539	-0.268815
H	4.155059	3.659089	-0.276900
H	3.527253	2.299185	-1.216792
H	3.711044	2.150358	0.533366
C	1.598221	4.571988	1.523252
H	2.261637	5.437158	1.408234
H	1.916086	4.027230	2.415232
H	0.588128	4.955619	1.703054

M062X/6-311G(d): -641.7387752 a.u.
Point group: D_2
Cartesian coordinates:

C	-0.66221	1.41864	0.65829
C	-0.84681	1.31704	-0.67555
Si	0.00000	0.00000	-1.72965
Si	0.00000	0.00000	1.71241
C	-1.68650	2.32984	-1.44547
H	-1.43331	2.30940	-2.50979
H	-1.49117	3.35247	-1.10977
C	-1.06593	2.66924	1.43001
H	-1.18249	2.44142	2.49375

H	-2.03365	3.05550	1.09680
Si	-1.82157	-0.69207	3.04548
Si	1.82157	0.69207	3.04548
Si	1.57105	1.17117	-3.04149
Si	-1.57105	-1.17117	-3.04149
C	0.79002	2.60770	-3.99206
H	-0.06971	2.30221	-4.59372
H	1.53062	3.03878	-4.67300
H	0.46161	3.40451	-3.32023
C	2.37478	0.04377	-4.32982
H	1.63850	-0.27170	-5.07512
H	2.82033	-0.85770	-3.90389
H	3.16464	0.58127	-4.86359
C	-0.79002	-2.60770	-3.99206
H	-1.53062	-3.03878	-4.67300
H	-0.46161	-3.40451	-3.32023
H	0.06971	-2.30221	-4.59372
C	-1.30395	-1.99962	4.30988
H	-2.18111	-2.36568	4.85258
H	-0.62419	-1.56804	5.05050
H	-0.80587	-2.86567	3.86842
C	-2.56812	0.73671	4.03500
H	-3.30340	0.34239	4.74356
H	-3.08608	1.45108	3.39060
H	-1.81989	1.28705	4.61101
C	-3.18467	-1.33851	1.91239
H	-4.06917	-1.62947	2.48707
H	-2.87528	-2.19734	1.31344
H	-3.48553	-0.55074	1.21470
C	1.30395	1.99962	4.30988
H	0.80587	2.86567	3.86842
H	2.18111	2.36568	4.85258
H	0.62419	1.56804	5.05050
C	3.18467	1.33851	1.91239
H	3.48553	0.55074	1.21470
H	4.06917	1.62947	2.48707
H	2.87528	2.19734	1.31344
C	2.56812	-0.73671	4.03500
H	1.81989	-1.28705	4.61101
H	3.30340	-0.34239	4.74356
H	3.08608	-1.45108	3.39060
C	-3.18230	2.02162	-1.29930
H	-3.49394	2.06216	-0.25339
H	-3.41001	1.01846	-1.66526
H	-3.79025	2.73064	-1.86661
C	0.00000	3.76294	1.28386
H	-0.25749	4.64908	1.86930
H	0.11757	4.06388	0.24076
H	0.97232	3.40388	1.62735
C	0.66221	-1.41864	0.65829
C	0.84681	-1.31704	-0.67555
C	1.06593	-2.66924	1.43001
H	1.18249	-2.44142	2.49375
H	2.03365	-3.05550	1.09680
C	1.68650	-2.32984	-1.44547
H	1.49117	-3.35247	-1.10977
H	1.43331	-2.30940	-2.50979
C	0.00000	-3.76294	1.28386
H	-0.11757	-4.06388	0.24076
H	-0.97232	-3.40388	1.62735
H	0.25749	-4.64908	1.86930
C	3.18230	-2.02162	-1.29930
H	3.79025	-2.73064	-1.86661
H	3.49394	-2.06216	-0.25339
H	3.41001	-1.01846	-1.66526
C	-2.37478	-0.04377	-4.32982
H	-1.63850	0.27170	-5.07512
H	-2.82033	0.85770	-3.90389
H	-3.16464	-0.58127	-4.86359
C	-2.86258	-1.92717	-1.89102
H	-2.38270	-2.64973	-1.22378
H	-3.63274	-2.46041	-2.45664
H	-3.36000	-1.19043	-1.25751
C	2.86258	1.92717	-1.89102
H	3.36000	1.19043	-1.25751
H	2.38270	2.64973	-1.22378
H	3.63274	2.46041	-2.45664

1d: 1,1,4,4-Tetrasilyl-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene (ethyl groups with up-(Si)-down-up-(Si)-down conformation)

B3LYP/6-31G(d): 2213.49408 a.u.

Point group: D_2

Cartesian coordinates:

C	0.676803	-1.586291	0.056895
C	-0.676803	-1.586291	-0.056895
Si	-1.709999	0.000000	0.000000
Si	1.709999	0.000000	0.000000
C	-1.476276	-2.884241	-0.194044
H	-2.497468	-2.742604	0.181589
H	-1.040946	-3.673878	0.428340
C	1.476276	-2.884241	0.194044
H	2.497468	-2.742604	-0.181589
H	1.040946	-3.673878	-0.428340
Si	3.128846	-0.149760	-1.896588
Si	3.128846	0.149760	1.896588
Si	-3.128846	-0.149760	1.896588
Si	-3.128846	0.149760	-1.896588

C	-1.556198	-3.378989	-1.651503
H	-0.560055	-3.589015	-2.055050
H	-2.021821	-2.632375	-2.303685
H	-2.152058	-4.296595	-1.716156
C	1.556198	-3.378989	1.651503
H	2.152058	-4.296595	1.716156
H	0.560055	-3.589015	2.055050
H	2.021821	-2.632375	2.303685
C	0.676803	1.586291	-0.056895
C	-0.676803	1.586291	0.056895
C	1.476276	2.884241	-0.194044
H	2.497468	2.742604	0.181589
H	1.040946	3.673878	0.428340
C	-1.476276	2.884241	0.194044
H	-1.040946	3.673878	-0.428340
H	-2.497468	2.742604	-0.181589
C	1.556198	3.378989	-1.651503
H	0.560055	3.589015	-2.055050
H	2.021821	2.632375	-2.303685
H	2.152058	4.296595	-1.716156
C	-1.556198	3.378989	1.651503
H	-2.152058	4.296595	1.716156
H	-0.560055	3.589015	2.055050
H	-2.021821	2.632375	2.303685
H	2.341261	-0.135323	-3.162922
H	4.094549	0.985716	-1.950713
H	3.924877	-1.410548	-1.870483
H	-4.094549	0.985716	1.950713
H	-2.341261	-0.135323	3.162922
H	-3.924877	-1.410548	1.870483
H	2.341261	0.135323	3.162922
H	3.924877	1.410548	1.870483
H	4.094549	-0.985716	1.950713
H	-3.924877	1.410548	-1.870483
H	-4.094549	-0.985716	-1.950713
H	-2.341261	0.135323	-3.162922

1e: 1,1,4,4-Tetrasilyl-1,4-disilacyclohexa-2,5-diene
B3LYP/6-31G(d): -1898.98746 a.u.
Point group: D_2
Cartesian coordinates:

C	-0.674949	0.000094	1.535398
C	0.674949	-0.000094	1.535398
Si	1.764436	0.000000	0.000000
Si	-1.764436	0.000000	0.000000
Si	-3.133934	1.925517	-0.000671
Si	-3.133934	-1.925517	0.000671
Si	3.133934	-1.925517	-0.000671
Si	3.133934	1.925517	0.000671
C	-0.674949	-0.000094	-1.535398
C	0.674949	0.000094	-1.535398
H	-2.308719	3.166291	-0.001132
H	-4.009616	1.949492	-1.207370
H	-4.010351	1.950338	1.205534
H	4.009616	-1.949492	-1.207370
H	2.308719	-3.166291	-0.001132
H	4.010351	-1.950338	1.205534
H	-2.308719	-3.166291	0.001132
H	-4.010351	-1.950338	-1.205534
H	-4.009616	-1.949492	1.207370
H	4.010351	1.950338	-1.205534
H	4.009616	1.949492	1.207370
H	2.308719	3.166291	0.001132
H	1.187158	0.000205	-2.502677
H	-1.187158	-0.000205	-2.502677
H	-1.187158	0.000205	2.502677
H	1.187158	-0.000205	2.502677

CCSD/6-31G(d): -452.7691126 a.u.
Point group: D_2
Cartesian coordinates:

C	-0.67731	-0.00000	1.53342
C	0.67731	0.00000	1.53342
Si	1.76462	0.00000	0.00000
Si	-1.76462	0.00000	0.00000
Si	-3.10759	1.92741	-0.00001
Si	-3.10759	-1.92741	0.00001
Si	3.10759	-1.92741	-0.00001
Si	3.10759	1.92741	0.00001
C	-0.67731	0.00000	-1.53342
C	0.67731	-0.00000	-1.53342
H	-2.25367	3.15017	0.00011
H	-3.98050	1.95253	-1.21016
H	-3.98070	1.95244	1.21000
H	3.98050	-1.95253	-1.21016
H	2.25367	-3.15017	0.00011
H	3.98070	-1.95244	1.21000
H	-2.25367	-3.15017	-0.00011
H	-3.98070	-1.95244	-1.21000
H	-3.98050	-1.95253	1.21016
H	3.98070	1.95244	-1.21000
H	3.98050	1.95253	1.21016
H	2.25367	3.15017	-0.00011
H	1.18622	-0.00001	-2.50453
H	-1.18622	0.00001	-2.50453
H	-1.18622	-0.00001	2.50453
H	1.18622	0.00001	2.50453

1f: 1,1,4,4-Tetramethyl-1,4-disilacyclohexa-2,5-diene
B3LYP/6-31G(d): -893.50189 a.u.
Point group: D_2
Cartesian coordinates:

C	-0.674722	0.000035	1.529635
C	0.674722	-0.000035	1.529635
Si	1.769548	0.000000	0.000000
Si	-1.769548	0.000000	0.000000
C	0.674722	0.000035	-1.529635
C	-0.674722	-0.000035	-1.529635
C	-2.876849	1.539092	0.000131
H	-2.281333	2.458890	0.000140
H	-3.524968	1.559319	0.884937
H	-3.525231	1.559479	-0.884474
C	-2.876849	-1.539092	-0.000131
H	-3.524968	-1.559319	-0.884937
H	-3.525231	-1.559479	0.884474
H	-2.281333	-2.458890	-0.000140
C	2.876849	-1.539092	0.000131
H	3.525231	-1.559479	-0.884474
H	2.281333	-2.458890	0.000140
H	3.524968	-1.559319	0.884937
C	2.876849	1.539092	-0.000131
H	2.281333	2.458890	-0.000140
H	3.524968	1.559319	-0.884937
H	3.525231	1.559479	0.884474
H	1.184253	0.000087	-2.500697
H	-1.184253	0.000087	2.500697
H	-1.184253	-0.000087	-2.500697
H	1.184253	-0.000087	2.500697

1g: 1,1,4,4-*Tetrakis*(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene
B3LYP/6-31G(d): -2370.89627 a.u.
Point group: D_2
Cartesian coordinates:

C	-1.528095	-0.003154	0.675704
C	-1.528095	0.003154	-0.675704
Si	0.000000	0.000000	-1.785881
Si	0.000000	0.000000	1.785881
Si	-0.006973	-1.965500	3.130351
Si	0.006973	1.965500	3.130351
Si	-0.006973	1.965500	-3.130351
Si	0.006973	-1.965500	-3.130351
C	-1.739029	2.243641	-3.868812
H	-2.053640	1.405714	-4.501385
H	-1.753397	3.150401	-4.487170
H	-2.492373	2.367962	-3.082070
C	1.248200	1.822312	-4.554598
H	1.006257	0.99338	-5.230292
H	2.267085	1.661431	-4.182649
H	1.257584	2.743215	-5.151930
C	1.739029	-2.243641	-3.868812
H	1.753397	-3.150401	-4.487170
H	2.492373	-2.367962	-3.082070
H	2.053640	-1.405714	-4.501385
C	1.248200	-1.822312	4.554598
H	1.257584	-2.743215	5.151930
H	1.006257	-0.993386	5.230292
H	2.267085	-1.661431	4.182649
C	-1.739029	-2.243641	3.868812
H	-1.753397	-3.150401	4.487170
H	-2.492373	-2.367962	3.082070
H	-2.053640	-1.405714	4.501385
C	0.453109	-3.478311	2.074583
H	0.458021	-4.392293	2.682504
H	1.448688	-3.366067	1.629709
H	-0.260032	-3.625242	1.255428
C	-1.248200	1.822312	4.554598
H	-2.267085	1.661431	4.182649
H	-1.257584	2.743215	5.151930
H	-1.006257	0.993386	5.230292
C	-0.453109	3.478311	2.074583
H	0.260032	3.625242	1.255428
H	-0.458021	4.392293	2.682504
H	-1.448688	3.366067	1.629709
C	1.739029	2.243641	3.868812
H	2.053640	1.405714	4.501385
H	1.753397	3.150401	4.487170
H	2.492373	2.367962	3.082070
C	1.528095	0.003154	0.675704
C	1.528095	-0.003154	-0.675704
C	-1.248200	-1.822312	-4.554598
H	-1.006257	-0.993386	-5.230292
H	-2.267085	-1.661431	-4.182649
H	-1.257584	-2.743215	-5.151930
C	-0.453109	-3.478311	-2.074583
H	0.260032	-3.625242	-1.255428
H	-0.458021	-4.392293	-2.682504
H	-1.448688	-3.366067	-1.629709
C	0.453109	3.478311	-2.074583
H	1.448688	3.366067	-1.629709
H	-0.260032	3.625242	-1.255428
H	0.458021	4.392293	-2.682504
H	-2.500038	0.006185	-1.181976
H	-2.500038	-0.006185	1.181976
H	2.500038	-0.006185	-1.181976
H	2.500038	0.006185	1.181976

6: Cyclohexa-1,4-diene
B3LYP/6-31G(d): - 233.41645 a.u.
Point group: D_{2h}
Cartesian coordinates:

C	-0.667430	-1.255229	0.000000
H	-1.207534	-2.201120	0.000000
C	0.667430	-1.255229	0.000000
H	1.207534	-2.201120	0.000000
C	1.500211	0.000000	0.000000
H	2.177769	0.000000	-0.870804
H	2.177769	0.000000	0.870804
C	0.667430	1.255229	0.000000
H	1.207534	2.201120	0.000000
C	-0.667430	1.255229	0.000000
H	-1.207534	2.201120	0.000000
C	-1.500211	0.000000	0.000000
H	-2.177769	0.000000	-0.870804
H	-2.177769	0.000000	0.870804

CCSD/6-311G(d): - 55.41894473 a.u.
Point group: D_{2h}
Cartesian coordinates:

C	-0.66981	-1.25727	0.00000
H	-1.20630	-2.20724	0.00000
C	0.66981	-1.25727	0.00000
H	1.20630	-2.20724	0.00000
C	1.50545	0.00000	0.00000
H	2.17674	0.00000	-0.87384
H	2.17674	0.00000	0.87384
C	0.66981	1.25727	0.00000
H	1.20630	2.20724	0.00000
C	-0.66981	1.25727	0.00000
H	-1.20630	2.20724	0.00000
C	-1.50545	0.00000	0.00000
H	-2.17674	0.00000	-0.87384
H	-2.17674	0.00000	0.87384

5: *para*-xylylene
B3LYP/6-31G(d): - 233.41645 a.u.
Point group: D_{2h}
Cartesian coordinates:

C	-0.02968	-0.13019	1.18117
C	0.21720	1.30891	3.15898
C	-1.60488	-0.37006	3.05331
C	-0.93585	0.68792	3.80761
C	-1.18274	-0.75117	1.82980
C	0.63933	0.92779	1.93547
H	-1.69996	-1.54175	1.29096
H	1.50079	1.40760	1.47658
H	0.73442	2.09949	3.69782
H	-2.46633	-0.84986	3.51220
C	0.39385	-0.51256	-0.04639
H	-0.10826	-1.29974	-0.60139
H	1.25172	-0.04657	-0.52252
C	-1.35939	1.07029	5.03517
H	-0.85728	1.85747	5.59017
H	-2.21726	0.60430	5.51130

CCSD/6-311G(d): -73.51876227 a.u.
Point group: D_{2h}
Cartesian coordinates:

C	-0.02840	-0.13134	1.17746
C	0.22388	1.31538	3.15989
C	-1.61191	-0.37622	3.05342
C	-0.93714	0.68907	3.81132
C	-1.18942	-0.75765	1.82889
C	0.64637	0.93395	1.93536
H	-1.70859	-1.54994	1.29009
H	1.50967	1.41555	1.47673
H	0.74305	2.10767	3.69869
H	-2.47521	-0.85782	3.51205
C	0.39478	-0.51340	-0.04909
H	-0.10859	-1.30184	-0.60432
H	1.25402	-0.04624	-0.52529
C	-1.36032	1.07113	5.03787
H	-0.85695	1.85957	5.59310
H	-2.21956	0.60398	5.51407

7
B3LYP/6-31G(d): -2372.1204792 a.u.
Point group: C_2
Cartesian coordinates:

C	-0.01081	-0.67621	1.51501
C	0.01081	0.67621	1.51501
Si	0.01081	-1.79091	-0.01575
Si	-0.01081	1.79091	-0.01575
C	0.38933	-0.66985	-1.53097
H	0.18196	-1.23125	-2.45359
C	-0.38933	0.66985	-1.53097
H	-0.18196	1.23125	-2.45359
Si	1.74900	-3.38946	0.27335
Si	-2.10958	-2.85222	-0.24438
Si	2.10958	2.85222	-0.24438
Si	-1.74900	3.38946	0.27335
C	3.45029	-2.56210	0.06218
H	4.25551	-3.28390	0.25124
H	3.58284	-1.72484	0.75671
H	3.58816	-2.17406	-0.95402
C	3.52788	1.61782	0.04581

H	4.50028	2.12377	-0.01308
H	3.52673	0.81328	-0.69839
H	3.45126	1.15138	1.03472
C	-3.45029	2.56210	0.06218
H	-3.58816	2.17406	-0.95402
H	-4.25551	3.28390	0.25124
H	-3.58284	1.72484	0.75671
C	-3.52788	-1.61782	0.04581
H	-3.52673	-0.81328	-0.69839
H	-3.45126	-1.15138	1.03472
H	-4.50028	-2.12377	-0.01308
C	1.66199	-4.14171	2.01960
H	2.45724	-4.88522	2.15947
H	0.70381	-4.64189	2.20070
H	1.78742	-3.37441	2.79267
C	1.61883	-4.79650	-1.00312
H	2.44830	-5.50467	-0.87917
H	1.66226	-4.41478	-2.03014
H	0.68521	-5.36148	-0.89812
C	-2.29973	-4.26288	1.02170
H	-1.56507	-5.06060	0.86073
H	-3.29754	-4.71418	0.94540
H	-2.17954	-3.90277	2.05043
C	-2.29101	-3.58364	-1.99337
H	-1.51607	-4.32963	-2.20464
H	-2.22112	-2.80654	-2.76380
H	-3.26549	-4.07570	-2.10788
C	2.29973	4.26288	1.02170
H	3.29754	4.71418	0.94540
H	2.17954	3.90277	2.05043
H	1.56507	5.06060	0.86073
C	2.29101	3.58364	-1.99337
H	3.26549	4.07570	-2.10788
H	1.51607	4.32963	-2.20464
H	2.22112	2.80654	-2.76380
C	-1.66199	4.14171	2.01960
H	-0.70381	4.64189	2.20070
H	-1.78742	3.37441	2.79267
H	-2.45724	4.88522	2.15947
C	-1.61883	4.79650	-1.00312
H	-0.68521	5.36148	-0.89812
H	-2.44830	5.50467	-0.87917
H	-1.66226	4.41478	-2.03014
H	-0.02637	-1.17978	2.48842
H	0.02637	1.17978	2.48842
H	-1.46967	0.46993	-1.54357
H	1.46967	-0.46993	-1.54357

8

B3LYP/6-31G(d): -1302.1578245

Point group: C_1

Cartesian coordinates:

C	-1.29668	0.07287	2.82447
C	-1.45574	0.08289	1.49111
Si	0.00000	0.00000	0.30056
Si	0.12601	2.00572	-0.96498
Si	-0.12601	-2.00572	-0.96498
C	-1.38064	2.19743	-2.11281
H	-1.43070	1.39550	-2.85855
H	-1.33272	3.15079	-2.65468
H	-2.32126	2.18588	-1.54956
C	1.70815	2.04803	-2.02286
H	1.72678	1.23866	-2.76207
H	2.60868	1.95355	-1.40458
H	1.78149	2.99751	-2.56863
C	1.38064	-2.19743	-2.11281
H	1.33272	-3.15079	-2.65468
H	2.32126	-2.18588	-1.54956
H	1.43070	-1.39550	-2.85855
C	1.29668	-0.07287	2.82447
C	1.45574	-0.08289	1.49111
C	-1.70815	-2.04803	-2.02286
H	-1.72678	-1.23866	-2.76207
H	-2.60868	-1.95355	-1.40458
H	-1.78149	-2.99751	-2.56863
C	-0.15789	-3.47374	0.24377
H	0.74267	-3.48815	0.86835
H	-0.21092	-4.42879	-0.29455
H	-1.02263	-3.41807	0.91500
C	0.15789	3.47374	0.24377
H	1.02263	3.41807	0.91500
H	-0.74267	3.48815	0.86835
H	0.21092	4.42879	-0.29455
H	-2.47850	0.13991	1.11414
H	-2.17816	0.12161	3.46963
H	2.47850	-0.13991	1.11414
H	2.17816	-0.12161	3.46963
C	0.00000	0.00000	3.59223
H	-0.04863	-0.86489	4.27684
H	0.04863	0.86489	4.27684

9

B3LYP/6-31G(d): -1303.3846339 a.u.

Point group: C_2

Cartesian coordinates:

C	-1.29373	-0.06386	2.84521
C	-1.41671	-0.04332	1.50629
Si	0.06747	-0.06668	0.34196
Si	0.12043	1.95670	-0.90476
Si	-0.04564	-2.01646	-1.00723
C	-1.56545	2.26296	-1.73455
H	-1.82904	1.46292	-2.43611
H	-1.55330	3.20579	-2.29658
H	-2.36946	2.33108	-0.99231
C	1.45993	1.90378	-2.25724
H	1.25386	1.12558	-3.00173
H	2.45343	1.70565	-1.83772
H	1.51093	2.86316	-2.78816
C	1.56173	-2.24851	-2.00093
H	1.51849	-3.16935	-2.59675
H	2.43572	-2.32183	-1.34292
H	1.73628	-1.41500	-2.69096
C	-1.50390	-1.92749	-2.22813
H	-1.39468	-1.09450	-2.93273
H	-2.45988	-1.79809	-1.70707
H	-1.57084	-2.85147	-2.81690
C	-0.28903	-3.53772	0.11079
H	0.55625	-3.67475	0.79573
H	-0.38019	-4.45211	-0.48954
H	-1.19506	-3.44295	0.71997
C	0.48939	3.42786	0.24604
H	1.47420	3.33595	0.71900
H	-0.25729	3.50628	1.04462
H	0.47830	4.37106	-0.31543
H	-2.43066	-0.05190	1.10117
H	-2.19500	-0.10570	3.46296
C	0.00131	-0.04537	3.62781
H	0.22810	-1.07150	3.96260
H	-0.15817	0.52716	4.55225
C	1.22104	0.53098	2.88940
H	1.04004	1.59661	2.69433
H	2.08784	0.48524	3.56377
C	1.54543	-0.19005	1.56534
H	2.46156	0.22334	1.12442
H	1.75936	-1.24821	1.77320

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