

UV/Vis Spectroscopy

Electronic Transitions in Conformationally Controlled Tetrasilanes with a Wide Range of SiSiSiSi Dihedral Angles

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Abstract: Unlike π -electron chromophores, the peralkylated *n*-tetrasilane σ -electron chromophore resembles a chameleon in that its electronic spectrum changes dramatically as its silicon backbone is twisted almost effortlessly from the *syn* to the *anti* conformation (changing the SiSiSiSi dihedral angle ω from 0 to 180°). A combination of UV absorption, magnetic circular dichroism (MCD), and linear dichroism (LD) spectroscopy on conformationally controlled tetrasilanes 1–9, which cover fairly evenly the full range of angles ω , permit-

ted a construction of an experimental correlation diagram for three to four lowest valence electronic states. The free chain tetrasilane *n*-Si₄Me₁₀ (**10**), normally present as a mixture of three enantiomeric conformer pairs of widely different angles ω , has also been included in our study. The spectral trends are interpreted in terms of avoided crossings of 1B with 2B and 2A with 3A states, in agreement with SAC-CI calculations on the excited states of 1–7 and conformers of **10**.

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Introduction

Spectral effects of π -electron delocalization have been investigated extensively, but much less is known about the delocalization of σ electrons, although it is ubiquitous in main group element frameworks of both saturated and unsaturated compounds, and surely affects their photophysical properties.

Polysilanes and oligosilanes Si_nR_{2n+2}, which contain a singly bonded chain of silicon atoms with lateral organic substituents, represent an accessible and convenient model for the study of σ delocalization. They have drawn much attention as potential electronic and photonic materials due to their distinctive optical and electronic properties, such as UV absorption,^[1–8] luminescence,^[5–9] non-linear polarizability,^[10,11] and photoconductivity,^[12] and the results have been reviewed repeatedly.^[13–20] One of their most striking features is thermochromism,^[21] believed to be primarily due to a conformational dependence of their absorption spectra.^[22–26] In solutions of unconstrained permethylated silicon chains, the favored SiSiSiSi dihedral angles ω are approximately 165° (*transoid*), 55° (*gauche*), and 90° (*ortho*), whereas in chains carrying longer substituents, values of approximately 150° (*deviant*) are also common, and values of about 40° (*cisoid*) are possible.^[20,27–29] In most cases, the thermodynamically favored conformations with a large number of *transoid* dihedral angles become predominant at lower temperatures.^[30] These conformers generally show the effects of σ delocalization most strongly and absorb at longer wavelengths, whereas the smallest SiSiSiSi dihedral angles act as defects and hinder an effective display of the effects of conjugation.^[31,32]

Much effort has been devoted to the investigation of these conformational effects in chains of various lengths. These studies have been both computational (ladder C model,^[33–36] con-

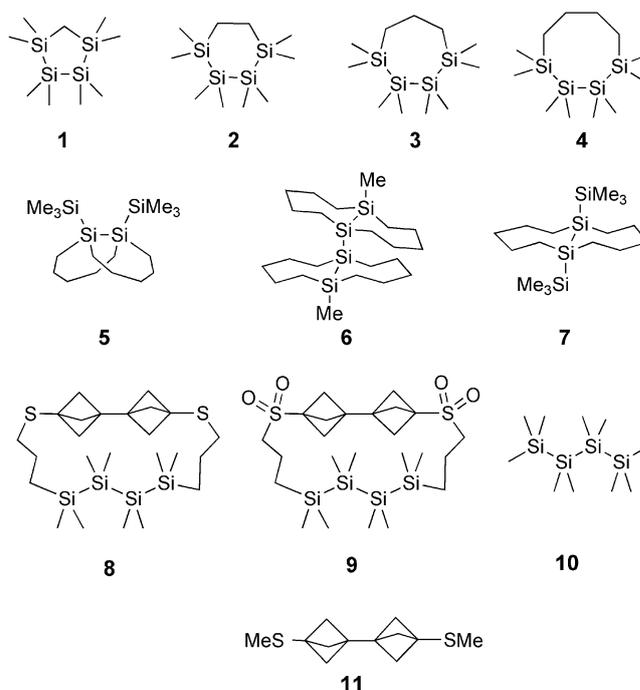
formational analysis,^[27,28,37–41] excited state calculations on n - Si_4H_{10} ,^[42–44] n - $\text{Si}_4\text{Me}_{10}$ (**10**),^[33,45–47] and longer chains^[32] and experimental (matrix isolation of n - $\text{Si}_4\text{Me}_{10}$ conformers,^[45,48] conformational control based on cyclic carbosilanes,^[6,8,48–51] bicyclic disilanes,^[31,51–55] bicyclic trisilane,^[56,57] and bulky lateral substituents,^[58] hypervalent silicon,^[59–62] helicity induction by chiral terminal^[63–65] or lateral^[66,67] substituents, and inclusion into cyclodextrin and other hosts^[68–73]).

n -Tetrasilanes such as **10** have been frequently employed as model compounds,^[6,8,45–47,49,50] since they are the shortest oligosilanes that exhibit backbone conformational isomerism. Their backbone possesses a two-fold axis of symmetry and their states can transform according to A or B irreducible representations. Transitions from the 1A ground state into A states, polarized along the symmetry axis that runs perpendicular to the central SiSi bond in the chain, are usually weak. Transitions into B states, polarized perpendicular to the symmetry axis, are often strong, especially if their polarization direction parallels the central SiSi bond. The traditional belief was that in oligosilane chains of all lengths an increase of ω toward 180° causes the excitation energy of the first transition to decrease. Tetrasilanes are anomalous, however,^[45,46] as in this case it is not so much the excitation energy as the oscillator strength of low-energy electronic transitions that changes with ω . The reason for this anomaly is believed to be the proximity of the excitation energies of the lowest strongly allowed $\sigma\sigma^*$ and very weak $\sigma\pi^*$ transitions in extended conformations of short chains. Strictly speaking, the $\sigma\sigma^*$ and $\sigma\pi^*$ labels apply only to the $\omega = 0^\circ$ and 180° limits, in which a plane of symmetry is present, but a generalization has been proposed.^[32] In long chains the $\sigma\sigma^*$ excitation is clearly lower in energy. In tetrasilanes, the $\sigma\sigma^*$ and $\sigma\pi^*$ excitations produce the 1B and 2B states, which undergo an avoided crossing as ω goes from 0° to 180° . At $\omega = 0^\circ$, 2B corresponds to the intense $\sigma\sigma^*$ transition and 1B to the weak $\sigma\pi^*$ transition, and the opposite is true at $\omega = 180^\circ$, for reasons easily understood in terms of the simple ladder C model.^[48] Between the two limits, the two B states are allowed to mix and their crossing is avoided. The behavior of transitions into these states is reflected in the UV spectra of matrix-isolated conformers of the parent permethylated tetrasilane and of peralkylated tetrasilanes whose conformation has been intentionally controlled.^[6,45,46,49,50,52,53] The situation is even more complicated, since in the vicinity of the *syn* geometry ($\omega = 0^\circ$) an avoided crossing with yet another state of B symmetry takes place.^[18,33,46]

Calculations further indicate the existence of two weakly allowed low-energy excited states of A symmetry, and 1B, 2B, 2A, and 3A comprise the four lowest energy singlet excited states.^[34] The 2A state is calculated to be the lowest of these for the *ortho* and *gauche* conformers of n - $\text{Si}_4\text{Me}_{10}$ and to be 0.1 eV above the 1B state in the *transoid* conformer.^[46] The 2A state could thus play an important role in tetrasilane photochemistry and photochemistry.^[74] For a comprehensive understanding of low-energy excitations of this chromophore, one should therefore detect all four calculated low-energy states and construct an experimental “correlation diagram” in which their course is traced as a function of ω over its whole range.

Much of the previous work suffered from limited coverage of angles larger than 90° and from band overlap, which made it difficult to trace all low-energy transitions independently. However, such a diagram has been published for ionization potentials, that is, within the limitations of Koopman’s theorem, for energies of the occupied molecular orbitals (MOs).^[51]

In the present paper, we report UV, MCD, and LD spectra of conformationally controlled tetrasilanes **1–9** (Scheme 1), which



Scheme 1. Compounds studied in this paper.

nearly evenly cover the range $0^\circ \leq \omega \leq 180^\circ$, since we have included the tetrasilanes **5–7**, and the free-chain permethylated tetrasilane n - $\text{Si}_4\text{Me}_{10}$ (**10**). The results provide a first complete experimental characterization of the peralkylated n -tetrasilane chromophore by displaying the conformational dependence of transitions to 2A, 1B, and 2B states over the full range of ω . Some experimental evidence for the predicted transition 3A is also presented. Spectral interpretations are supported by ab initio calculations by the symmetry-adapted cluster-configuration interaction (SAC-CI) method.

The MCD spectra of **1–4**, **8**, and **10** have been reported in a short communication,^[6] as have the MCD and LD of **6**.^[53] The disulfone **9** and bis(methylthio)[2]staffane (**11**) are included in order to deal with potential complications from sulfur atom based excitations in the spectra.

Experimental Section and Calculations

Materials

Tetrasilanes **1–4**,^[50] **5–7**,^[52] **8** and **9**,^[8] and **10**^[75] were prepared as reported and purified thoroughly either by preparative GC (**1–4**), distillation (**5**), recrystallization (**6** and **7**), or multiple runs of semi-preparative HPLC (**8** and **9**). 3,3'-Di(methylthio)[2]staffane (**11**) was prepared and purified as previously reported.^[76] 3-Methylpentane (Phillips) and cyclopentane (Fisher) were extracted with concentrated sulfuric acid, distilled from Na, and then purified on a column of silver nitrate impregnated alumina.^[77] 2-Methylbutane (isopentane) and hexanes were used as received from Aldrich. UV/Vis and MCD spectra of compounds **1–4** and **10** were measured in hexane solution, **5–7** in 3-methylpentane, and **8** in a 3:7 isopentane/cyclopentane mixture. The disulfone **9** was measured in acetonitrile (HPLC grade), as it is not soluble in alkanes.

UV Absorption

UV absorption spectra were recorded with a Cary 17 spectrometer (**1–4**), or with an OLIS RSM 1000 spectrometer (**5–10**). The spectrometers were calibrated against a holmium oxide filter. Sample solutions with concentrations of approximately 10^{-5} M were used for the measurements in a 10 mm pathlength Suprasil quartz cell. For measurement of low-temperature spectra, the samples were contained in Suprasil cells immersed in liquid nitrogen in a quartz Dewar vessel equipped with Suprasil windows.

Magnetic circular dichroism (MCD)

The spectra were recorded at room temperature with a JASCO J720 spectrometer in the presence of a magnetic field (1.5 T) parallel to the propagation direction of light with approximately 10^{-5} M sample solutions in a 1 cm-pathlength CD quality (strain-free) cell. The magnetic field was calibrated using an aqueous solution of Co^{II} sulfate hydrate.^[78,79]

Linear dichroism (LD)^[80]

The LD mode of a JASCO J500C spectrometer was employed to measure the dichroism of solutes absorbed in stretched polyethylene sheets, known from previous work to be uniaxial with respect to the stretching direction *Z* (i.e., *Y* and the light propagation direction *X* are equivalent). The instrument measures directly both the difference of absorbances of *Z*-polarized and *Y*-polarized light $LD = E_Z - E_Y$ and the average absorbance $E_{XY} = (E_Z + E_Y)/2$. In some cases, we show the plots of LD and in others we found it more instructive to plot the reduced dichroism $LD_r = LD/E_{XY}^{iso} = 3LD/(E_Z + 2E_Y)$, in which the isotropic absorbance was taken from ordinary solution spectra, neglecting the difference in solvent effects between a saturated hydrocarbon and polyethylene.

Commercial polyethylene sheets were cut into $\approx 2 \times 2$ cm pieces and soaked in spectral grade chloroform for several hours before use to remove additives. The purified sheet was soaked in a chloroform solution of a tetrasilane, washed with MeOH to remove crystals from the surface, dried overnight, and stretched ≈ 400 – 600 %. For **4**, **8** and **10** the stretched sheet was rinsed with CHCl₃ and allowed to dry, then rinsed with either spectral grade MeOH or EtOH and dried before blank spectra were measured. The stretched sheet, still clamped in the stretcher, was placed in a CHCl₃ saturated chamber at least 30 min prior to application of the compound. A saturated solution of the compound in CHCl₃ was applied dropwise to the center of the stretched sheet, which was then returned

to the CHCl₃-saturated chamber. After a period of time ranging from approximately 1 to 24 h, depending on the compound, during which the compound dissolved into the sheet, the sheet was removed from the chamber and allowed to dry. Rinsing with either MeOH or EtOH removed any compound that remained on the surface of the sheet. Measurements were made after the sheet dried for a minimum of 1 h. In order to reduce the effects of light scattering, the sample sheet was located as close as possible to the photomultiplier tube.

Calculations

Ground-state geometries of **1–7** and **10** were optimized using density functional theory (DFT) with the B3LYP functional^[81] and 6–311G(d) basis set.^[82,83] For **10**, partial optimization was also carried out with a fixed angle ω ranging from 0° to 180° in increments of 15° and all the other coordinates optimized.

At these geometries, the energies and oscillator strengths of excitation into low-lying valence states of **1–7** and **10** were calculated using the SAC-CI method^[84–87] and the McLean and Chandler^[83] valence triple zeta [6s5p] plus [1d] polarization function with $\zeta_d = 0.262$ for Si and Huzinaga–Dunning^[88] double zeta [4s2p/2s] for C and H atoms as the basis set. The number of basis functions ranged from 246 to 416 (Supporting Information). The SD-*R* method was adopted, in which single (S) and double (D) excitations are used for *R* operators. In the SAC-CI calculation, the 1s, 2s, and 2p orbitals of Si, 1s orbital of C, and their counterparts in the virtual orbitals were frozen as core. The resultant active space was 39–75 occupied and 178–299 unoccupied MOs. We employed the direct SAC-CI algorithm with all nonlinear terms.^[89] The perturbation selection method^[90] was adopted for the linear terms with an energy threshold of $\lambda_g = 10^{-6}$ au and $\lambda_e = 10^{-7}$ au. The SAC/SAC-CI dimensions were 200 000–300 000/400 000–500 000 after the perturbation selection (see Supporting Information for additional detail). All calculations were performed with the development version of the Gaussian09 suite of programs.^[91]

Results

Measurements and calculations

UV absorption and MCD spectra are shown in Figure 1. Simultaneous fitting of absorption and MCD curves provided the singlet transition energies, intensities, and B terms given in Table 1, which also shows the proposed attributions to calculated transitions. Since the real shapes of the absorption and MCD peaks are not necessarily Gaussian, and since the shapes of absorption and MCD envelopes of an electronic transition need not be identical, the fitting process is not fully reliable. In a few cases, we were forced to depend on subjective judgment of what are true transitions and what are merely corrections due to non-Gaussian band shapes. Peaks located significantly above $50\,000\text{ cm}^{-1}$ by the fitting were considered unreliable and are not listed. Linear dichroism in stretched polyethylene is shown in Figures 2 (**5–7**) and 3 (**4**, **8**, and **10**), and in Figure S1 (Supporting Information). The tetrasilanes **1–3** did not orient sufficiently for a meaningful LD measurement.

SiSiSiSi dihedral angles ω in the tetrasilanes **1–7** were obtained from B3LYP/6–311G(d) optimized geometries (Table 1, Table S1 and Figure S2 in the Supporting Information). The ground-state potential energy curve of **10** obtained by B3LYP/

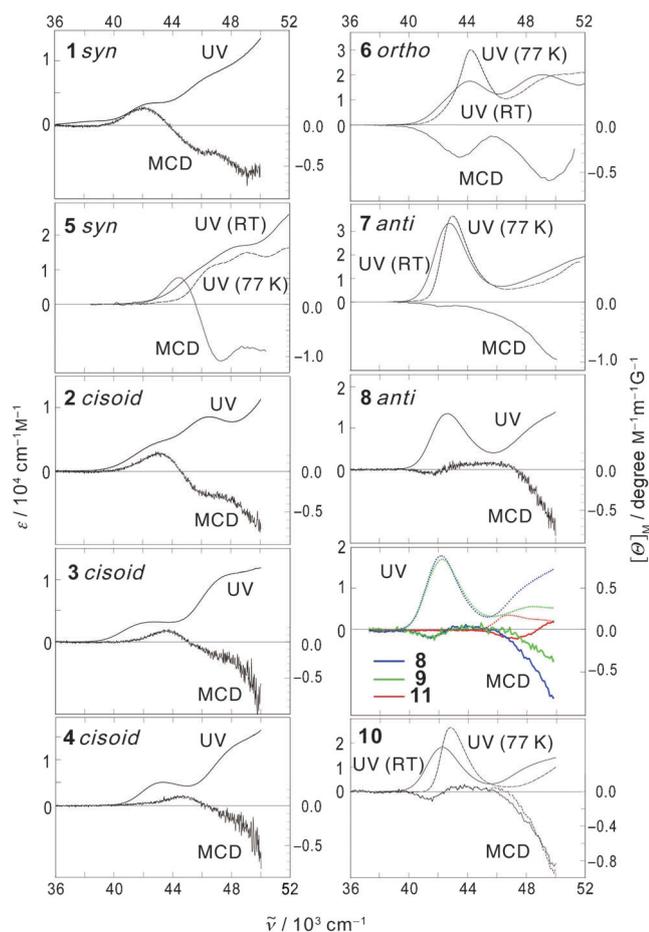


Figure 1. UV and MCD spectra of 1–11, arranged in the increasing order of calculated dihedral angles ω : $\approx 0^\circ$ (1), $\approx 15^\circ$ (5), $\approx 45^\circ$ (2), $\approx 55^\circ$ (3), $\approx 70^\circ$ (4), $\approx 100^\circ$ (6), $\approx 165^\circ$ (10), $\approx 180^\circ$ (7–9).

6–311G(d) optimizations constrained to fixed values of ω and the energies of the orbitals HOMO-1 to LUMO + 1 are shown in Figure 4. The Supporting Information displays the MOs at various dihedral angles (Figure S3), SAC-CI dimensions (Table S2), and detailed SAC-CI results (Tables S3–S5).

Figure 5 compares the SAC-CI calculated spectra of 1–4 with those of 10 that have similar dihedral angles. Table S6 and Figure S4 (Supporting Information) give the SAC-CI excitation energies and oscillator strengths of the ten lowest energy transitions for 15° increments in ω from 0 to 180° . For ω between 0 and 45° , the HOMO→LUMO transition to the 1B state is $\sigma_1\pi^*$ in character and the HOMO-1→LUMO + 1 transition into the 2B state is $\sigma_2\sigma^*$. Between 60 and 105° , the HOMO→LUMO + 1 transition is into the 1B state and $\sigma_1\pi^*$ in character, whereas the HOMO-1→LUMO transition is into the 2B state and $\sigma_2\sigma^*$ in nature. Between 120 and 180° , the transitions are HOMO→LUMO $\sigma_1\sigma^*$ into the 1B state and HOMO-1→LUMO + 1 $\sigma_2\pi^*$ into the 2B state. The state character exchange occurs between ω of 105 and 120° , where σ^* and π^* orbitals undergo an avoided crossing (Table S7 in the Supporting Information). Generally in linear organosilanes, $\sigma\pi^*$ transitions have lower oscillator strength and $\sigma\sigma^*$ transitions have higher intensity, but for ω between 105 and 120° the relative oscillator

strengths are reversed. The exchange of oscillator strength between transitions into 1B and 2B states occurs in the same region of dihedral angles ω .

Plots of the calculated singlet excitation energy and the oscillator strength of 10 against the calculated SiSiSiSi dihedral angle are shown in Figure 6. The calculated and measured absorption spectra of 5–7 are compared in Figure 7.

Based on the results of the previous *ab initio*^[50,51] and the present DFT calculations, we assume that the geometrical differences among the silicon backbones of the possibly many conformers of each of the compounds 1–4 are small. The calculated dihedral angles ω among the conformers of each molecule vary at most by approximately 20° , less than the difference between the *gauche* and the *ortho* conformer in 10. The two calculated SiSiSi valence angles δ lie between 100 and 117° (cf. the range 110 – 114° calculated for the conformers of the open-chain tetrasilane 10.^[46]

Assignments

For the *syn* tetrasilane 1, four unambiguous transitions were detected previously.^[6] The lowest-energy transition appears as an absorption band at $38\,600 \text{ cm}^{-1}$ with a very weak negative MCD (positive B term, hardly visible in Figure 1). This, and the third transition at $46\,100 \text{ cm}^{-1}$ with a much stronger negative MCD band, are assigned to A' -symmetry excited states by comparison with the SAC-CI calculations (Table 1), whereas the second band detected by absorption and positive MCD at $42\,200 \text{ cm}^{-1}$ is assigned to an A'' -symmetry excited state ($1A''$), and the fourth at $50\,300 \text{ cm}^{-1}$ to the $2A''$ state. The weak transition at almost the same energy ($49\,300 \text{ cm}^{-1}$) that also resulted from the spectral fitting but does not have a calculated counterpart may well be an artifact due to a non-Gaussian shape of the fourth transition. The transition energies agree very well with those calculated, except for the second transition, which is calculated about 2000 cm^{-1} too high.

The absorption spectrum of 5, with $\omega \approx 15^\circ$, is very similar to that of 1, but slightly blueshifted (Figure 1). This fits the slight blueshift observed in its photoelectron spectrum.^[51] Like the first ($1A \rightarrow 2A'$) transition in 1, the first transition of 5 at $42\,000 \text{ cm}^{-1}$ is again very weak and is best recognized through its positive LD (Figure 2), whose sign may well be dictated by vibronic intensity borrowing and cannot be used to assign excited state symmetry reliably. Analogy to 1 suggests that this excitation is to the 1B state. The same analogy would attribute the much more intense absorption shoulder near $47\,500 \text{ cm}^{-1}$, particularly clear in the low-temperature spectrum, with a negative MCD sign, to a transition to the 2B state. Between these two transitions, another transition at $45\,000 \text{ cm}^{-1}$ is identified by its strongly positive MCD and is assigned to the $2A$ state due to its close similarity to the transition to the $1A''$ state in 1. The transition to the $3A$ state is apparent at approximately $49\,000 \text{ cm}^{-1}$ in the low-temperature spectrum.

The agreement with the SAC-CI results is again essentially perfect. The calculations position the transitions to the $2A$, $3A$, and $2B$ states at almost the same energy near $47\,000 \text{ cm}^{-1}$, and place the first transition to the 1B state significantly lower

Table 1. Excited states of conformationally controlled tetrasilanes **1–9** and *n*-Si₄Me₁₀ (**10**).^[a]

Cmpd.	ω	Sym.	Conform.	Experimental			SAC-CI				
				$\bar{\nu}$ [10 ³ cm ⁻¹] ^[a]	<i>f</i>	<i>B</i> [10 ² β _e /cm ⁻¹]	$\bar{\nu}$ [10 ³ cm ⁻¹]	<i>f</i>	Assignment		
1	0	C _s	<i>syn</i>	38.6	0.0095	0.4	38.0	0.001	2A'	σ ₁ π*	
				42.2	0.035	-4.9	44.2	0.001	1A''	σ ₂ π*	
				46.1	0.098	9.4	46.3	0.085	3A'	σ ₁ σ*	
5	15	C ₂	<i>syn</i>	50.3	0.25	29	50.6	0.23	2A''	σ ₂ σ*	
				42	0.0077	-0.4	44.4	0.016	1B	σ ₁ π*	
				45	0.03	-21	46.7	0.041	2A	σ ₂ π*	
							46.9	0.039	3A	σ ₁ σ*	
							47.4	0.23	2B	σ ₂ σ*	
2	45	C ₂	<i>cisoid</i>	47.5	0.24	45					
				48.4	0.019	-9					
				42	0.026	0.3	42.7	0.03	1B	σ ₁ π*	
				43.2	0.034	-5.9	46.3	0.017	2A	σ ₁ σ*	
				46.0	0.073	4.5	46.7	0.053	3A	σ ₂ π*	
3	55	C ₂	<i>gauche</i>	47	0.072	2.8					
				50	0.11	11	48.9	0.192	2B	σ ₂ σ*	
				41.6	0.03	0	42.1	0.051	1B	σ ₁ π*	
				43.5	0.024	-3	46.1	0.018	2A	σ ₁ σ*	
				46.8	0.066	3.9	48.3	0.039	3A	σ ₂ π*	
4	70	C ₂	<i>gauche</i>	48.7	0.071	(-16.0?)	51.3	0.32	2B	σ ₂ σ*	
				[43	0.059	-0.7] ?					
				44.6	0.011	-1.4	44.5	0.089	1B	σ ₁ π*	
							47.5	0.012	2A	σ ₁ σ*	
				47.9	0.16	-1.2	49.7	0.036	3A	σ ₂ π*	
6	100	C ₁ (C ₂)	<i>ortho</i>	51.7	0.25	2B					
				42.9	0.0094	(-2.9?)	44.3	0.08	3A (2A)	σ ₂ π*	
				43.9	0.22	9.7	43.3	0.243	2A (1B)	σ ₁ σ*	
				45.5	0.053	-4.3	46.9	0.023	4A (3A)	σ ₂ σ*	
							48.1	0.054	5A (2B)	σ ₂ π*	
7	180	C _{2h}	<i>anti</i>	48.5	0.29	11	49.7	0.148	6A (3B)	σ ₃ σ*	
				50.1	0.042	4.9	50.2	0.076	7A (3A)	σ ₃ π*	
				42.9	0.34	0.9	43	0.41	1B _u	σ ₁ σ*	
				44.5	0.067	0.2	46	0.01	2B _u	σ ₂ σ*	
				48	0.14	14	48.1	0.001	1A _u	σ ₁ π*	
8	180	<i>anti</i>	53.8	0.072	2A _u						
			41.4	0.008	1.5						
			42.2	0.17	-0.3						
			43.8	0.05	-0.6						
9	<i>anti</i>	48	0.081								
		41	0.0013	0.4							
		42	0.18	1							
		43.8	0.02	-0.1							
		44.9	0.065	-1.5							
10 ^[b]	55 (g), 95 (o), 165 (t)		48.2	0.058	1.7						
			41.9	0.014	0.9	44.6 (t)	0.46	1B	σ ₁ σ*		
			42.7	0.14	-0.3	44.9 (o)	0.19	1B	σ ₁ π*		
			44.5	0.022	0.2	45.0 (t)	0.005	2A	σ ₁ π*		
			46.3	0.035	-4.5	50.7 (g)	0.248	2B	σ ₂ σ*		
	48.6	0.079	(-1.7)	52.6 (t)	0.019	2B	σ ₂ σ*				
				52.8 (t)	0.027	3B	σ ₃ σ*				

[a] Obtained by simultaneous fitting of absorption and MCD spectra with Gaussian components. Transitions significantly above the 50000 cm⁻¹ limit of observation have been deleted as unreliable. In a few cases weak components were treated as corrections to strong bands and not as independent transitions. Point symmetry group is stated in the left column (symbols in parentheses refer to approximate symmetry). A full list of fitting results is given in the Supporting Information. [b] The calculated values list all transitions of the majority conformer *t* and intense transitions of the minority conformers *g* and *o*.

at 44400 cm⁻¹. This agrees with the analogy to **1** drawn above.

As the SiSiSiSi dihedral angle ω increases in **1–4**, the label of the very weak 1A'→2A' transition becomes 1A→1B and it

gradually increases in intensity and blueshifts. The second transition is now labeled 1A→2A and its intensity and the corresponding positive MCD signal become weaker. The third band in the region of 46000–48000 cm⁻¹, assigned as a superposition of transitions to 2B and 3A states, apparently keeps its oscillator strength almost constant.

The spectra of **2** and **3** are very similar to that of **4** and do not need to be described separately. Three transitions in **4** have been assigned previously:^[6] 1) 1A→1B at 43000 cm⁻¹, 2) 1A→2A, whose presence is most easily discerned at approximately 44600 cm⁻¹ in the MCD spectrum (Figure 1), and 3) 1A→2B, located near 47900 cm⁻¹. Additional support for the assignment of transitions at these energies is provided by the LD_r values shown in Figure 3. The 1A→1B transition is clearly polarized along the principal orientation axis in stretched polyethylene, presumably approximately along the central SiSi bond, and appears at the energy reported earlier.^[49] A weak transition to the 2A state, polarized along the two-fold symmetry axis, appears as a valley in the LD_r plot in the region of the positive MCD peak. The strong 1A→2B transition that corresponds to the shoulder at 47900 cm⁻¹ in the E_{YZ} spectrum is polarized approximately parallel to the 1A→1B transition. It appears shifted to lower energy in the LD_r curve, because of overlap with one or more higher energy transition polarized perpendicular to the orientation axis. The existence of this transition, which has a strong positive MCD B term,^[6] is evident in the LD_r spectrum, although the peak maximum lies above the observed spectral range. Results of MS-CASPT2 calculations^[46] of transitions in the *o*_± and *g*_± conformers of **10** suggest that this is the 1A→2B transition, based on the high intensity and polarization direction.

The presence of a transition near 43000 cm⁻¹, the low energy onset of the first absorption peak, is apparent in LD_r curve (Figure 3). Reduction of the LD spectrum using the Thulstrup–Eggers–Michl (TEM) method^[80] also indicated the presence of a weak peak at approximately 43000 cm⁻¹, polarized perpendicular to the orientation axis. It is not at all apparent in absorption or MCD spectra and has not been identified previously. It is somewhat questionable since the LD_r curve is the only evidence for its existence and no transition at such a low energy appears in the SAC-CI results. If real, this transition has to be assigned to the 1A→2A state, based on the polarization and the same assignment of a transition at approximately 42900 cm⁻¹ in **6**, which is constrained to a SiSiSiSi ω of approximately 100°. ^[53] Then, the transition at 44600 cm⁻¹ would have to be reassigned to the 3A state. An alternative, and in our opinion more likely correct, interpretation of the observed sharp drop in LD_r of **4** near 41000 cm⁻¹ is to postulate that this absorption is due to

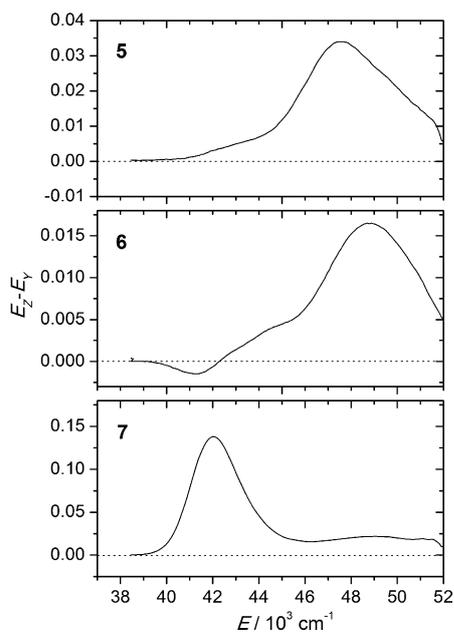


Figure 2. Linear dichroism $E_z - E_y$ of 5–7 in stretched polyethylene.

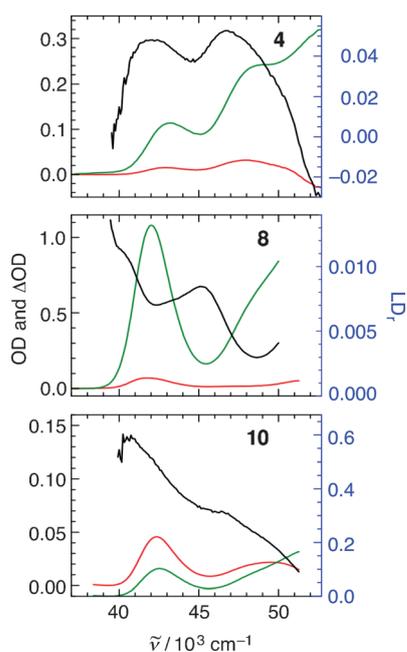


Figure 3. Spectra of 4, 8, and 10 in stretched polyethylene. Black, LD_i ; green, E_{yz} ; red, $E_z - E_y$. The green curve for 10 has been displaced vertically by 0.01.

a slightly redshifted $1A \rightarrow 1B$ transition in another conformer whose principal orientation axis is perpendicular to that in the principal conformer. Figure 8 shows that a temperature decrease causes a blueshift and narrowing of the first and second bands of 4, suggesting that a number of conformers with similar dihedral angles ω are present at room temperature, and that a change in the population distribution occurs upon cooling. A mixture of conformers is likely to be present in 4 even

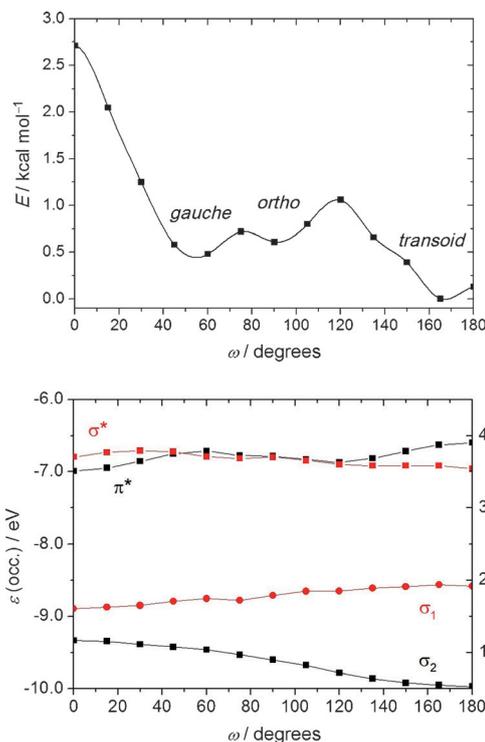


Figure 4. B3LYP/6-311G(d) results for 10. Top: Ground state potential energy curve. Bottom: Energies of HOMO-1 to LUMO+1.

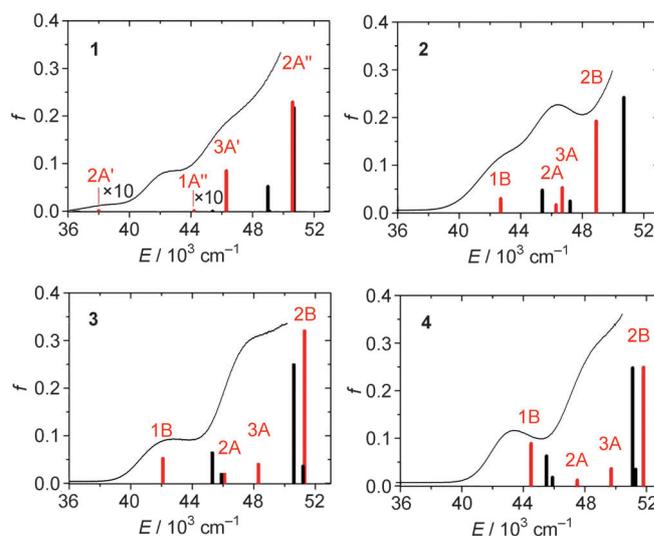


Figure 5. Comparison of SAC-Cl excitations in 1–4 (red bars) and in 10 (black bars) at the same dihedral angle ω . Observed spectra of 1–4 are shown for comparison.

in an aligned sample, and the calculated small differences in their intensities and transition dipole moment directions^[46] make the assignment of transitions difficult. Because of these doubts, Table 1 lists the possible transition at approximately 43000 cm^{-1} in brackets with a question mark. In its absence, the agreement between the observations and SAC-Cl calculations for 2–4 would be quite reasonable.

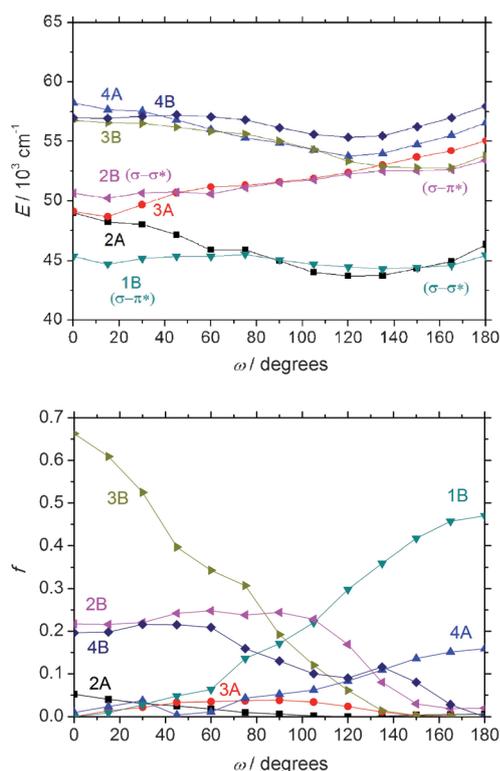


Figure 6. SAC-Cl computed transition energy (top) and oscillator strength (bottom) of **10** as a function of ω .

In **6** with $\omega \approx 100^\circ$, two transitions of nearly equal moderate intensity were detected by UV and MCD at energies similar to those of the transitions to B states in **4**, and were assigned to transitions into states of B symmetry.^[50] However, fitting of the spectra revealed six contributions and we suspect that a range of dihedral angles are accessible in solution at room temperature. One weak negative LD band and a weak shoulder are observed at 41 000–43 000 cm^{-1} (Figure 2), slightly below the 1B transition located at approximately 44 000 cm^{-1} , and we assign them to the 2A transition. The spectra of **6** are quite compatible with the SAC-Cl results (Table 1).

Upon further increase in the SiSiSiSi dihedral angle up to the *anti* limit ($\omega = 180^\circ$) in **7**, an intense UV absorption peak, with an oscillator strength of 0.34, appears in the low-energy region (42 900 cm^{-1}). This intense peak is unambiguously attributable to the transition into the excited 1B state with $\sigma\sigma^*$ character. The LD of **7** (Figure 2) contains a similar peak shifted to a somewhat lower energy, which strongly suggests that another differently polarized transition is hidden under the intense 1B band. We suspect that this is a transition into the 2A state, although its relatively low energy is not reproduced by SAC-Cl calculations. It is also discernible in MCD of **7–9** as a very weak negative peak. In **8** and **9** at least some of the intensity of this peak could be due to the presence of minor amounts of a twisted conformer, suggested by studies of the temperature dependence of fluorescence and fluorescence excitation spectra.^[8] Cooling causes a narrowing and a slight blue shift of the first band of **8** and a loss of most of the intensity of the

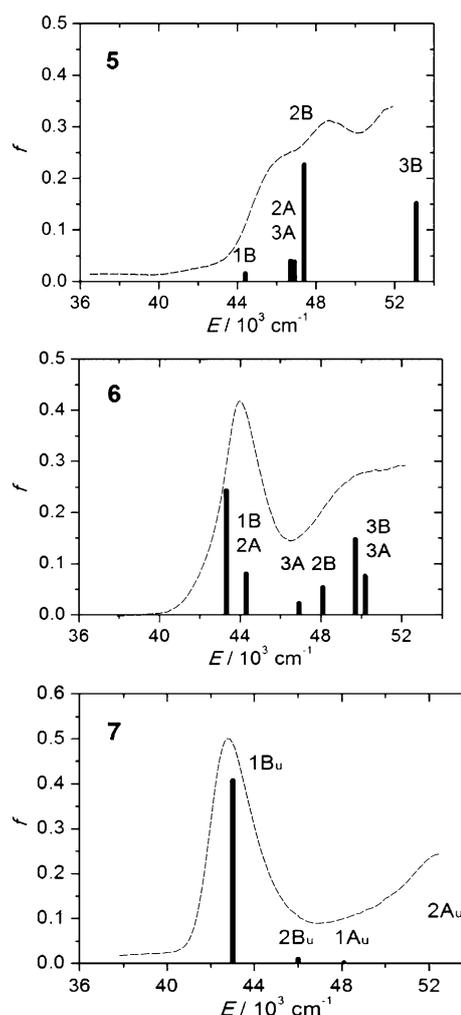


Figure 7. Observed and SAC-Cl computed absorption spectra of **5–7**.

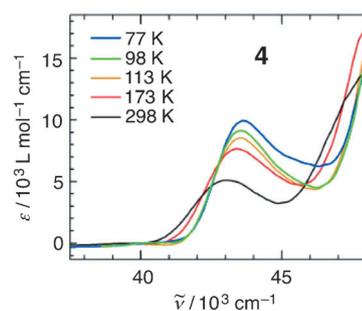


Figure 8. Temperature dependence of the UV absorption spectrum of **4**.

second band. This behavior is attributed to a decrease in the population of twisted (*ortho*) conformers at low temperatures. However, in **7** the presence of another conformer can be excluded, and at least in this compound the peak must be due to another electronic transition into a state that we assigned above as 2A. The SAC-Cl calculation did not provide an assignment for this peak.

As shown in Figure 1, MCD reveals a negative peak under the first absorption band of **8**, followed by a weak broad positive peak at higher energy. To verify that both features are due to the tetrasilane chromophore and do not involve the sulfur lone pairs, the absorption and MCD spectra of **11** are also shown. They have no intensity until 45 000 cm^{-1} , at which point a positive MCD B term begins. Figure 1 also makes it clear that the absorption and MCD spectra of **8** and **9** are very similar up to 47 000 cm^{-1} , above which the end absorption in the spectrum of **9** has a weak positive MCD B term, and we conclude that all spectral features below approximately 46 000 cm^{-1} are due to the tetrasilane chromophore. The negative MCD peak near 42 000 cm^{-1} in both **8** and **9** is in agreement with the presence of twisted conformers such as $8o_{\pm}$. The LD_r of **8** (Figure 3) confirms the presence of the two transitions identified from the MCD spectrum.^[6] Reduction of the LD spectra by the TEM method^[80] clearly indicated one transition at 41 400 cm^{-1} , polarized parallel to the principal orientation axis and assigned to the 2A state, and a second stronger transition at 42 200 cm^{-1} into the 2B state polarized perpendicular, both at the same energy, as determined earlier by MCD. Two additional transitions above 45 000 cm^{-1} can be discerned from the LD results. A perpendicular polarized transition at approximately 48 500 cm^{-1} seen as a dip corresponds to 1A→2B. A hint of a parallel polarized transition may be seen in the LD_r curve at approximately 50 000 cm^{-1} . Both of these transitions lie in the region of a strong negative MCD peak (positive B term). The intensity of the solution absorption peak at approximately 48 500 cm^{-1} decreases with temperature (Figure 1). This molecule has an approximately square shape and does not appear to have a strong preference for orientation in stretched polyethylene: a stretched sheet containing **8** with a maximum optical density of 1.0 at 42 200 cm^{-1} yielded a maximum LD value of only 0.1.

The spectra of **10**, especially the low-temperature absorption, strongly resemble those of **7–9** and are clearly dominated by its *transoid* conformer and its 1A→1B transition. The transition to the 2A state observed in the MCD spectrum of **10** is not evident from the LD_r curve (Figure 3). Instead there is a steady decrease in LD_r from the absorption onset at approximately 40 000 cm^{-1} to 45 000 cm^{-1} that we believe is due to the presence of six transitions, one each of A and B symmetry from the t_{\pm} , g_{\pm} and o_{\pm} conformers, under the first absorption

band. The second band in the E_{YZ} spectrum is dominated by transitions of A symmetry, most likely to an A state of the t_{\pm} and o_{\pm} conformers, as these transitions are calculated to have moderate intensity.

The results for the 1B and 2B states of all the tetrasilanes are summarized in Figure 9 in the form of experimental state and transition intensity correlation diagrams for the peralkylated *n*-tetrasilane chromophore from $\omega=0$ to 180°. There is too much uncertainty in the oscillator strengths and to a lesser extent also the energies of the generally weaker and overlapping 2A and 3A states to attempt a similar correlation.

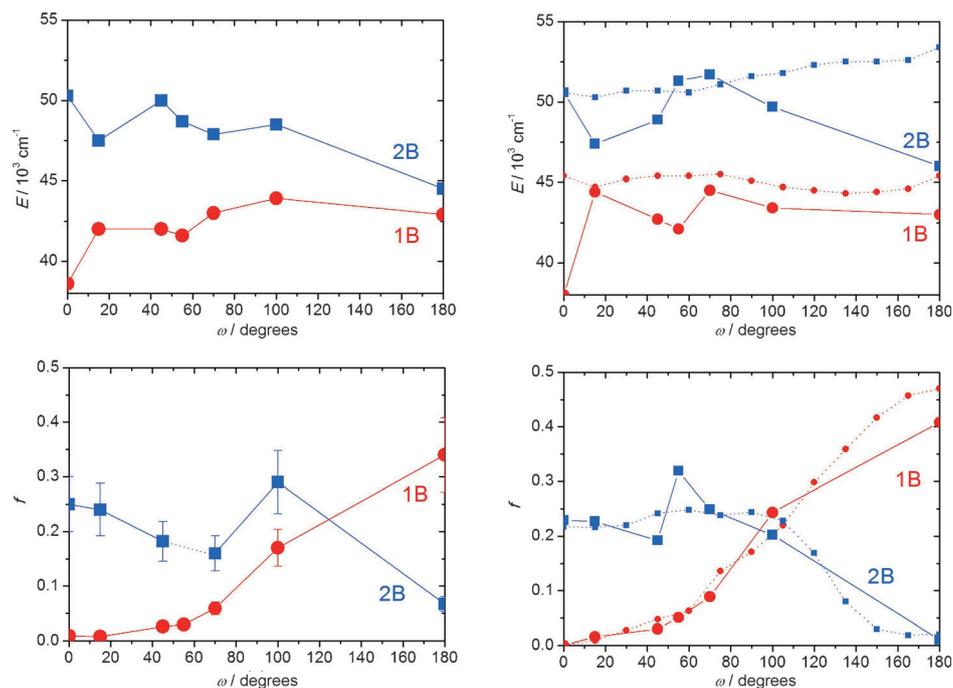


Figure 9. Experimental (left, from measurements on **1–7**) and SAC-Cl computed (right, from calculations on **1–7** in full lines and from calculations on **10** in dashed lines) correlation diagrams for tetrasilane excited state energies (top) and oscillator strengths (bottom) of transitions to the 1B and 2B states between $\omega=0$ and 180°.

Discussion

Conformational dependence of electronic transitions

We assume that the exact nature of the alkyl substituents has only a minor effect on the electronic states of the peralkylated tetrasilane chromophore, and that they merely serve as a passive scaffold that defines the silicon backbone conformation. This assumption is clearly least well satisfied in the case of **1**, where cyclic hyperconjugation through the methylene group undoubtedly affects the excitation energies measurably. It is further proposed that the calculated transitions of all the conformers that contribute to the spectra of each of the tetrasilanes **1–9** are similar enough to each other in band energy and intensity that they merely broaden the observed bands and that the variation in valence angles only plays a secondary role. Then, the observed spectra represent good approximations for generic *n*-tetrasilanes with dihedral angles ω that range from about 0 to 180°. This proposal is based on the fol-

lowing evidence: 1) Matrix isolation IR spectra suggested that two or more conformers are present in the case of **2–4**, but when matrices containing one of the cyclic oligosilanes **1–4** were irradiated at any one of two or three different wavelengths to achieve partial photodecomposition into a trisilane and dimethylsilylene, all their UV and also IR spectral features lost intensity at the same rate within experimental error, suggesting that all conformers present had very similar UV absorption spectra.^[50,51] Matrix annealing did not reveal the presence of conformers with distinctly different IR spectra, a sign that they are structurally closely related (or that high energy barriers prevent an interconversion, which appears unlikely). 2) Results of calculations based on a thorough conformational search^[8] suggest that no low-energy conformers have been overlooked. All conformers of any one of the tetrasilanes have nearly identical calculated SiSiSi valence angles and IR intensity patterns. In each one, the range of their SiSiSiSi dihedral angles, which have undoubtedly the most influence on the absorption spectra, is much smaller than the overall range within the series. 3) The assumption that the geometrical differences among the distinct conformers of **1–4** must be small is also supported by their photoelectron spectra,^[51] which exhibit sharper features than those of **10**, as expected for a narrower range of dihedral angles ω .

A ring flip of **5** may allow its dihedral angle to vary in the range $\approx -30^\circ < \omega < \approx 30^\circ$. A variable temperature ¹³C NMR spectroscopy study of the bis(tetramethylene) analogue revealed that the ring flip did not stop even at -90°C .^[52] The most stable conformer of **6** found among several likely conformations tested computationally was found to be *ortho*,^[53] and the present results agree that it is unlikely that it could be *anti*. The geometry of **7** is rigidly constrained to an *anti* conformation.^[52]

The transition energies are less sensitive to the lateral alkyl group length than the ionization potentials,^[51] and this facilitates the comparisons. Calculations on both Si₄H₁₀ and **10** place four singlet transitions into the easily accessible UV region, two into states of A symmetry and two into states of B symmetry.^[42–44] As transitions into A states of rod-shaped chromophores with a symmetry axis perpendicular to the chain have an intrinsically lower transition probability in one photon absorption spectroscopy, the B states are the ones most likely to be observed. The calculated excitation energies of these two lowest transitions into B states are almost independent of ω whereas their oscillator strengths vary significantly. At $\omega = 180^\circ$ the transition into the 1B (B_u) state is $\sigma\sigma^*$ and strongly allowed whereas the transition into the 2B (B_g) state is $\sigma\pi^*$ and has no intensity.^[6] For $\omega = 0^\circ$ the opposite is true. The transition into the 2B state (B₂) is now $\sigma\sigma^*$ and strongly allowed, and the transition into the 1B (B₁) state is $\sigma\pi^*$ and very weak. For intermediate values of ω both transitions are calculated to have fairly high intensities, with transition into 2B being stronger at $\omega < 120^\circ$. According to calculations, this behavior is due to an avoided crossing between the two lowest B states as the dihedral angle ω is varied from 180 to 0° . One of the two transitions into A states also is of the $\sigma\sigma^*$ and the other of the $\sigma\pi^*$ type, and they are predicted to undergo a similar avoided

crossing as the B states. According to the calculations the first one shows some intensity only for dihedral angles ω below 30° , and the second is nearly degenerate with the 2B state.

The UV spectra show two to four distinct transitions between 35 000 and 50 000 cm⁻¹. The intensity pattern agrees well with the calculated behavior. Absorption spectra of tetrasilanes with SiSiSiSi dihedral angles ω much lower than 90° are dominated by a strong transition into the 2B state near 50 000 cm⁻¹ and those with ω much larger than 90° are dominated by a strong transition into the 1B state near 42 000 cm⁻¹. When ω is close to 90° , the 1B and 2B states have comparable intensity. In all cases, other transitions appear in the spectra with smaller intensities and with rare exceptions cannot be resolved clearly, due to overlap with stronger transitions. Fortunately, MCD and LD spectra reveal unambiguously the presence of a third or even a fourth transition in most cases. MCD is particularly useful in that it shows a strong positive signal for the transition into the 2A state, which is weak in absorption. The MCD signal of the 2B state is strong and negative. In contrast, the MCD of the transition to the 1B state is almost unobservably weak except at ω near 90° . Other spectroscopic measurements, such as two photon absorption, could perhaps reveal the predicted 3A state and possibly further hidden transitions.

For molecules of C₂ symmetry, the highest found in linear tetrasilanes and the longer free chains, the electronic transition must be polarized either along the symmetry axis or in a direction perpendicular to it. The utility of LD spectroscopy is limited by uncertainties about the generally poor orientation properties of the tetrasilanes studied and by their low symmetry, which excludes the use of the most powerful interpretation tools.

It is interesting that the MCD and the LD spectra of **10** differ so much. It seems that in stretched polyethylene mainly the *transoid* conformer of **10** is aligned and contributes to the observed spectrum whereas in the MCD the *gauche* population provides much of the signal. Further experiments with longer oligosilanes are needed to establish whether this observation is generally valid. If so, these two techniques ought to yield new information about conformational equilibria in polysilane high polymers.

Overall, the agreement with the SAC-CI calculated course of energy and intensity is very good, and the qualitative trends are also reproduced by earlier calculations by less advanced methods mentioned in the Introduction.

State correlation diagram

A profound conformational dependence seems to be a hallmark of σ -electron chromophores, and at first sight, spectra of tetrasilanes differing in the dihedral angle ω have almost nothing in common. The present results demonstrate their underlying unity. They are summarized in Figure 9, in which the upper part shows the state energy and the lower part the transition oscillator strength correlation diagrams between the two extreme dihedral angles $\omega = 0^\circ$ and $\omega = 180^\circ$. We realize that the diagrams are imperfect in that the deviations of the SiSiSi va-

lence bond angles in the real compounds 1–7 from the model $n\text{-Si}_4\text{Me}_{10}$ surely are not without influence, and that the effects of the constraining alkane chains are not totally negligible (in particular, the state energies in 1 are undoubtedly lowered by the cyclic hyperconjugation in the five-membered ring). The anticipated effects of these factors are illustrated by the difference between the points on the full lines, calculated for the real structures 1–7, and the points on the dashed lines, calculated at a series of dihedral angles for the idealized structure 10. Overall, the diagram based on experimental data (left-hand side) agrees qualitatively with the calculated one (right-hand side).

Summary

UV absorption, MCD, and LD measurements allowed the detection of two to four transitions for each tetrasilane. The first two transitions into the B symmetry excited states were confirmed to obey the avoided crossing behavior. A transition into the 2A state was detected by MCD and LD, but the expected transition into the 3A state was hard to discern. The experimental data permitted the construction of a state correlation diagram between the $\omega = 0^\circ$ and $\omega = 180^\circ$ extremes, which ties together observations for seemingly entirely unrelated spectra of the peralkylated n -tetrasilane chromophore at different conformations.

anti-Tetrasilane exhibits only an insignificant MCD signal in the area of its UV absorption peak, whereas the signal from twisted tetrasilane conformations is strong. If this result holds for longer chains, MCD could be a powerful tool for the detection and characterization of twisted portions of polysilane chains.

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Keywords: conformational effects · electronic spectra · SAC-CI calculations · silicon · UV/Vis spectroscopy

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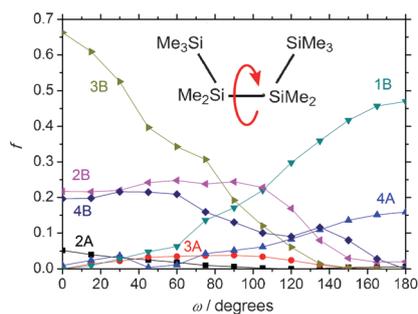
FULL PAPER

UV/Vis Spectroscopy

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Electronic Transitions in
Conformationally Controlled
Tetrasilanes with a Wide Range of
SiSiSiSi Dihedral Angles



Chemical chameleon: The facile rotation of $\text{Si}_4\text{Me}_{10}$ around the central SiSi bond transforms its absorption spectrum dramatically (calculated transition intensities are shown).