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UV, MCD, and LD Spectra of a Conformationally Constrained *ortho*-Tetrasilane: Support for the Avoided Crossing Model of Conformational Effects on Excited States[†]

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UV absorption, magnetic circular (MCD), and linear (LD) dichroism of an *n*-tetrasilane configurationally constrained to the ortho conformation (calculated SiSiSiSi dihedral angle $\omega \simeq 95$ °) are reported, and the results are compared with the theoretical expectation of four low-energy transitions. Two strong UV absorption maxima with similar intensity and positive MCD B terms are assigned to states of B symmetry. A third calculated transition to an 2^1A state was clearly detected in the LD spectrum, but a calculated weak transition to a 3^1A state at a higher energy was not observed. The results support a previous rationalization of the conformational properties of the *n*-tetrasilane chromophore, according to which one of two low-energy transitions into B-symmetry states is of $\sigma\sigma^*$ and the other of $\sigma\pi^*$ type in the planar cis and anti limits, and they undergo a strongly avoided crossing as ω changes from 0° to 180°, keeping their energies nearly constant but interchanging their oscillator strengths.

Introduction

Polysilanes containing SiSi single bonds[1] have many interesting properties attributable to σ delocalization within the silicon backbone. Their striking electronic absorption in the near UV region is solvatochromic[2] and thermochromic.[3] The characteristic red shift of a polysilane absorption maximum with decreasing temperature is usually attributed to a change in the conformation of the silicon backbone toward the all-anti limit,[4] but the exact conformations of the various forms are generally not known.

To understand the relation between spectral properties and conformation, many theoretical and experimental studies have been carried out, but even the shortest conformationally interesting case, *n*-tetrasilane, has not yet been definitively settled. Low-level ab initio calculations suggested that there are four low-energy valence states, two of A and two of B symmetry. Contrary to prior beliefs, they also suggested that it is not so much the energies as the oscillator strengths of the two strong transitions into B states that are functions of the SiSiSiSi dihedral angle ω.[5−8] Specifically, as ω increases, the oscillator strength of the transition into the 1^1B state ($\sigma\pi^*$ at 0° and $\sigma\sigma^*$ at 180°) would grow, while that of the transition into the 2^1B state ($\sigma\sigma^*$ at 0° and $\sigma\pi^*$ at 180°) would diminish. The intensities would be comparable when $\omega = 90-130°$. A recent high-level MS−CASPT2 calculation for the anti form of the parent tetrasilane Si_4H_{10} confirmed the earlier results for the lowest four valence states at this particular conformation, and their description in terms of simple one-electron excitations, important for orbital correlation concepts.[9] It also predicted the presence of two additional valence states below the first Rydberg state of the anti conformer, one of A and one of B symmetry. These, too, have simple Hückel analogues. It is not yet known whether similar two additional valence states will be predicted for peralkylated tetrasilanes, but it seems likely. Such high level calculations would be useful for confirming or refuting the avoided crossing model of conformational effects, but are difficult and have not yet been performed for tetrasilane conformations other than anti. Experimental data available so far are in agreement with the model, but are limited in scope.

Partial separation of individual conformer spectra deduced from the effects of annealing and selective photodecomposition of the conformers of *n*-Si_4H_{10}[7] (calculated to be anti, $\omega = 180°$, and gauche, $\omega \simeq 60°$) and *n*-Si_4Me_{10}[6] (separated spectrally into transoid, calculated at $\omega \simeq 165°$, and a mixture of gauche and ortho, calculated at $\omega \simeq 55°$ and 90°, respectively)[10] isolated in low-temperature matrices yielded information that was compatible with the avoided crossing proposal.[5−8] Stronger evidence was obtained[11] from the spectra of several tetrasilanes incorporated into five-to-eight-membered carbosilane ring systems, whose calculated dihedral angles ω ranged from 0 to 80°. However, a more definitive confirmation of the avoided crossing model would result from measurements on tetrasilane conformers in the so far unexplored central region of dihedral angles, $\omega \simeq 80-160°$, in much of which the avoided crossing would cause the two transitions to B symmetry states to have comparable predicted intensities.

The very recently communicated[12] syntheses of conformationally constrained syn, eclipsed,[13] and anti oligosilanes comprising a configurationally constrained disilane as a monomer building block offer such an opportunity. By analogy with a structurally very similar hexasilane whose central SiSi bond was found to be eclipsed[13] by single-crystal X-ray analysis, it was proposed that the central SiSi bond in the tetrasilane **1** (Figure 1) would be also eclipsed,[13] with $\omega \simeq 120°$, and is the first tetrasilane to feature a dihedral angle value within the previously unexplored central region. It was noted[12] that its UV absorption spectrum contained peaks at 229 and 204 nm (43700 and 49000 cm^{-1}) with almost identical intensity, as predicted,

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TABLE 1: Summary of Observed Spectra

	UV absorption			MCD			LD	
transition	$\tilde{\nu}$ (cm^{-1})	ϵ (M^{-1} L cm^{-1})	D (D^2)	$\tilde{\nu}$ (cm^{-1})	$[\Theta]_M$ (deg L M^{-1} m^{-1} G^{-1})	B (10^3 D^2 β_e/cm^{-1})	$\tilde{\nu}$ (cm^{-1})	sign
$1^1A \rightarrow 2^1A$							41 300	−
$1^1A \rightarrow 1^1B$	44 200	17 500	13.7	43 300	−0.34	0.77	44 700	+
$1^1A \rightarrow 2^1B$	49 100	20 100	17.5	49 600	−0.58	1.3	48 700	+

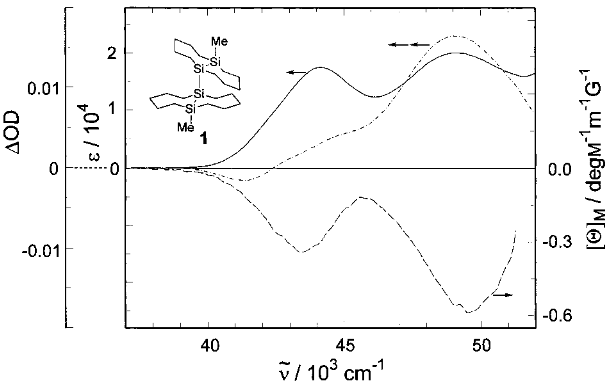

Figure 1. UV (—), MCD (- -), and LD (— • —) spectra of the *ortho*-tetrasilane **1** (upper part).

but the higher energy transition was barely recognized as an absorption peak. We have now examined the spectral properties of **1** more closely and have calculated its optimized geometry as well.

Experimental Part

Materials. The tetrasilane **1**[12,14] was purified by repeated recrystallization from hexane containing a little ethanol. 3-Methylpentane was purified by passage over silver nitrate on alumina column.[15] A commercial polyethylene sheet was soaked in chloroform for several hours in order to remove additives and dried before use. The purified sheet was soaked in a highly concentrated chloroform solution of **1** for 30 min, washed with methanol, dried overnight, and stretched to about 4 times its original length.

Spectral Measurements. 3-Methylpentane solution was used for UV absorption and MCD spectral measurements at ambient temperature. The former was measured with an OLIS RSM 1000 spectrometer and the latter with a JASCO J-500C spectrometer in the presence of 1.5 T of magnetic field parallel to the propagation direction of the light (100 scans taken at 5 nm/min with 4 s response time were averaged). The LD spectrum of the stretched polyethylene sheet was measured in the LD mode of the a JASCO J-500C spectrometer. All three measurements used a resolution of 0.5 nm.

Calculations. Ab initio optimization of the geometry of **1** with normal-mode frequency analysis was performed with IBM RS-6000-590 and HP Exemplar 2000 computers using the Gaussian98[16] program. The optimization was started at a point analogous to the X-ray structure[12] of a related hexasilane[17] and was performed successively at the HF/3-21G(d),[18] HF/6-31G-(d),[19] and B3LYP/6-31G(d) levels. The improvement in the level of calculation had a small effect on SiSi bond lengths (Si1−Si2 and Si3−Si4, 2.35, 2.37, and 2.37 Å, respectively; Si2−Si3, 2.42, 2.45, and 2.44 Å, respectively), and on the dihedral angle ω (99.6, 95.8, and 95.4°, respectively).

Results and Discussion

The tetrasilane **1** (Figure 1) was prepared and characterized according to a published procedure.[12] Unfortunately, an attempt to perform a single-crystal X-ray structure analysis of **1** failed, and the best available approximation to the molecular geometry is that provided by a DFT optimization. At the B3LYP/6-31G* level, the dihedral angle ω of the silicon backbone was calculated to be 95.4°, somewhat smaller than anticipated from a comparison with a related hexasilane.[12,17] This corresponds to the ortho conformation, and we now start referring to the tetrasilane **1** as ortho instead of eclipsed. Regardless of the exact value of the dihedral angle ω in **1**, it clearly lies in the previously unexplored central region.

The room-temperature UV absorption spectrum in 3-methylpentane is shown in Figure 1 and summarized in Table 1. Two strong and distinct absorption peaks are observed at 44200 cm^{-1} (ϵ = 17 500) and 49100 cm^{-1} (ϵ = 20 100), with dipole strengths D^{20} equal to 13.7 and 17.5 D^2, respectively, and fitting with Gaussians hints at the presence of an additional weak band near 41000 cm^{-1}.

The presence of two strong transitions of nearly equal intensity in this spectral range makes this tetrasilane unique among those studied so far. Those with smaller dihedral angles ω display two transitions, but the lower-energy one is much weaker than the higher-energy one,[6,11] while the spectrum of the anti conformer shows only one distinct peak in this energy region. The behavior observed presently fits very nicely the expectations based on the avoided crossing model[5−8] and the CIS/3-21G(d) calculations for n-Si$_4$Me$_{10}$,[8] permitting an assignment of the two peaks to transitions into the 1^1B and 2^1B states. The agreement with the expected intensities is not perfect in that at dihedral angles $\omega \simeq 95-100$ °, the calculated 2^1B oscillator strength is almost twice that of the 1^1B transition, but the CIS/3-21G(d) approximation is very crude, the calculation is for n-Si$_4$Me$_{10}$ rather than for **1**, and the accuracy of the HF and DFT geometry optimization for peralkylated oligosilanes is somewhat questionable, since substituent−substituent van der Waals interactions are not well described.[21]

At the limit of our instrumentation, above 52000 cm^{-1}, the absorption curve seems to rise again (Figure 1), and it is conceivable that this is an indication of the presence of yet another intense transition, perhaps analogous to the transition into the third valence state of B symmetry calculated[9] for Si$_4$H$_{10}$.

Additional information was sought from magnetic circular dichroism (MCD)[20] and linear dichroism (LD),[22] also shown in Figure 1 and summarized in Table 1. The transitions assigned to B states have positive MCD B terms (negative peaks), -0.77×10^3 D$^2\beta_e$/cm^{-1} for the 1^1B state and -1.3×10^3 D$^2\beta_e$/cm^{-1} for the 2^1B state, where β_e is the Bohr magneton. No additional transitions hidden in the UV spectrum are apparent, but it is curious that the first MCD peak is shifted significantly to lower energies relative to the first absorption peak. The simplest way to account for this would be to postulate the presence of two negative broad MCD peaks in this region, one at the position of the observed absorption peak and another weaker one at lower energies. In the absorption spectrum, the latter would then correspond to the weak and unresolved band whose presence was hinted at by the Gaussian fitting. The B term obtained by integration and given in Table 1 would then correspond to the sum of the B terms of both transitions.

The suspicion that an unresolved peak at lower energies is indeed present in the absorption and MCD spectra is confirmed by the linear dichroism (LD) of a sample dissolved in a stretched polyethylene sheet. This clearly reveals an additional transition near 41000−42000 cm^{-1}. In Figure 1 we plot $LD = E_Z - E_Y$, the difference of absorbance observed with the electric vector of plane polarized light oriented parallel and oriented perpendicular to the polymer stretching direction Z. Little is known about the orientation of molecules such as **1** in stretched polyethylene, and only a qualitative interpretation of the LD results can be offered. The molecular symmetry is C_2, restricting the possible directions of the molecular orientation axis and of molecular transition moments to two choices, either along the 2-fold symmetry axis or anywhere in the plane perpendicular to it. We assume that the LD of the intense absorption peaks assigned above as 1^1B and 2^1B is dictated by the directions of their transition moments, since overlap with absorption intensity due to other transitions appears to be negligible. If the assignment to transitions into B states is correct, these transition moments are perpendicular to the C_2 axis. The strongly positive LD signal of the transition assigned as 2^1B shows that its transition moment is inclined toward the principal molecular orientation axis, which is therefore also perpendicular to the C_2 axis, as might be expected from consideration of molecular shape. The lower positive LD intensity of the 1^1B transition, which is nearly equally strong in absorption, is surely in part due to overlap with the negative LD peak of the first transition. Even at the high-energy side, however, it is low, showing that the transition moment to the 1^1B state, although still inclined toward the principal orientation axis, forms a larger angle with it than the transition moment to the 2^1B state does.

Most important, a weak negative peak is observed near 41300 cm^{-1}, at the low-energy slope of the 1^1B absorption peak, where the absorption spectrum hinted at and the MCD spectrum more strongly suggested the presence of a weak transition masked by overlap with the strong 1^1B transition. Its negative LD would clearly be even more pronounced if it were not for this overlap. The transition moment of this weak transition is inclined strongly away from the molecular orientation axis. Although the measurement does not reveal whether it lies in the C_2 axis or perpendicular to it, this observation is certainly compatible with the result of the CIS/3-21G(d) calculation for Si_4Me_{10} at $\omega \simeq$ 95−100°,[8] which predicts a transition into a 2^1A state that lies very close to but slightly below the 1^1B state. Therefore, we propose to assign the weak transition at ~41300 cm^{-1} that is apparent in the LD, suspected in the MCD, and hardly revealed at all in the absorption spectrum as a transition into the 2^1A state, with a transition moment in the C_2 axis.

Conclusions

The spectroscopic properties of the *ortho*-tetrasilane **1** confirm the expectations based on the avoided crossing model of conformational effects on low-energy electronic transitions in peralkylated *n*-tetrasilanes. Even though it was originally derived from a very low level of ab initio theory,[5−8] this model can now be viewed as correct, at least for the two B states. The analogous avoided crossing of two A states has not yet been verified and only the lower A state seems to ever have been observed before, in rare instances.[11] It has now also been detected in **1**. It would be important to observe the predicted higher A state to confirm the correctness of the avoided crossing model for the A states as well, but spectral overlap makes it difficult.

The higher energy A and B valence states predicted recently[9] for parent Si_4H_{10} may have counterparts in the peralkylated series, but remain to be observed in any tetrasilane in a definitive fashion.

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