Review

Recent experimental and theoretical aspects of the conformational dependence of UV absorption of short chain peralkylated oligosilanes

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Abstract

Recent experimental and theoretical aspects of the conformation dependence of UV absorption of short chain peralkylated oligosilanes are surveyed. In the current interpretation of the conformational effect on tetrasilane electronic transitions it is not the excitation energy but the intensity of the lowest valence transitions that changes significantly as the SiSiSiSi dihedral angle varies. The latest synthetic advances have enabled us to constrain the conformation of silicon backbone in oligosilanes to some extent to provide strong experimental evidence for the theoretical proposals. A similar conformational effect has been found for a series of hexasilane conformers.
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1. Introduction

1.1. Historical background

In 1964 oligosilanes were found to absorb near ultraviolet light as a result of delocalization of Si–Si σ bonds (σ-delocalization) [1]. Afterwards soluble polysilanes [2] were prepared and their UV absorption spectra showed thermochromism [3] and related phenomena. This has introduced a concept of silicon backbone conformation dependence of σ-delocalization. It has been widely accepted that the 'trans' conformation effectively extends σ-delocalization and 'gauche' does not. Consequently, a 'trans' conformer of a tetrasilane was supposed to afford a first absorption maximum at longer wavelengths and a 'gauche' conformer at shorter wavelengths. However, σσ*–σπ* avoided crossing behavior of low-lying excited singlet states was later found for *n*-tetrasilane [4], and the simple red-shift model is not easily applicable to this shortest conformationally interesting homologue. In this manuscript, we will survey the recent advances in the understanding of conformational effects on the UV absorption of short chain oligosilanes such as tetra- and hexasilanes.

1.2. Conformation nomenclature

Traditionally, in polysilane chemistry the term 'trans' was used to denote a conformation with a large dihedral angle ($\omega > 90°$) and the term 'gauche' one with a small dihedral angle ($\omega < 90°$). However, this labeling is obviously insufficient to describe the additional various conformations which appear in polysilane backbones. Thus, in M_nX_{2n+2} linear chains, including polysilanes, several additional stable conformers have been found [5,6] and even the Prelog-Klyne nomenclature has proved to be inadequate to describe them. Therefore, a new conformation nomenclature [7] has recently been proposed (Fig. 1). The present manuscript employs these labels to describe oligosilane conformers.

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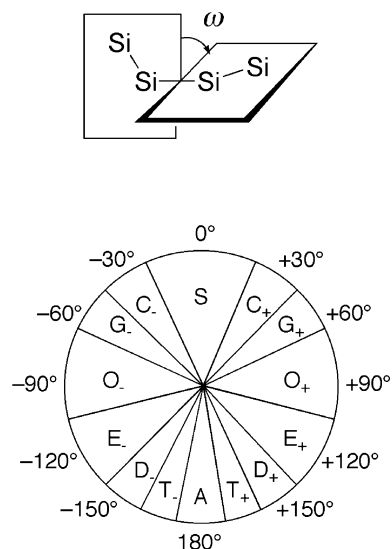*E-mail address:* tamao@scl.kyoto-u.ac.jp (K. Tamao).

Fig. 1. Suggested labels for linear chain conformers, where S–A stand for *syn, cisoid, gauche, ortho, eclipsed, deviant, transoid*, and *anti*, respectively.

2. Ladder C model [4,8]

Before discussing individual examples of the conformational effect, we introduce a model description of a σ-delocalized system and its conformation dependence. As shown in Fig. 2A, we consider four kinds of resonance integrals between sp^3 hybrid orbitals and label them β_{prim}, β_{gem}, β_{vic}, and $\beta_{1,3}$. The topology of orbital interactions is illustrated in Fig. 2B, and resembles the shape of a ladder. This inspired the authors to label this Huckel-type description the 'Ladder C model.' Addition of another silicon atom into the chain introduces additional β_{prim}, β_{gem}, β_{vic}, and $\beta_{1,3}$
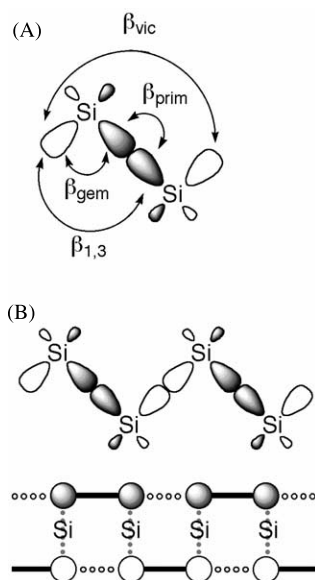

Fig. 2. (A) Transfer integrals between sp^3 hybrids in an oligosilane chain. (B) The topology of orbital interactions in HOMO: —, β_{prim}; ····, β_{gem}; ooo, β_{vic}.

integrals. One can easily recognize that β_{vic} is the only one among the four integrals that depends on silicon backbone conformation. In the all-*anti* conformation, the presence of β_{vic} with a positive value destabilizes the HOMO and stabilizes the LUMO. As the chain is twisted and becomes increasingly helical, β_{vic} gradually decreases and ultimately becomes negative. Its effect then is to stabilize the HOMO and destabilize the LUMO.

3. Tetrasilanes

3.1. Conformational effects on molecular orbital energies

The conformational effects on molecular orbital (MO) energies arising from the 1,4-orbital interaction β_{vic} are responsible for the conformational dependence of oligosilane photophysical properties. Fig. 3 shows an energy diagram of three high-energy occupied MOs (σ_1–σ_3) of a tetrasilane unit at the dihedral angle of 0° (*syn*) and 180° (*anti*). As the dihedral angle increases from 0 to 180°, the change in β_{vic} destabilizes the σ_1 and σ_3 orbitals and stabilizes the σ_2 orbital. Recent studies of photoelectron spectra of conformationally constrained tetrasilanes have provided experimental support for this expected tendency [9,10].

The unoccupied MOs which accept an electron from these occupied MOs in the process of electronic excitation are shown in Fig. 4. There are two types of MOs: (a) a σ* MO, which comprises silicon–silicon antibonding orbitals, and (b) a π* MO, which arises from silicon–carbon antibonding σ* orbital combinations possessing π symmetry with respect to a local SiSi plane. Their MO energies also show conformation dependence.
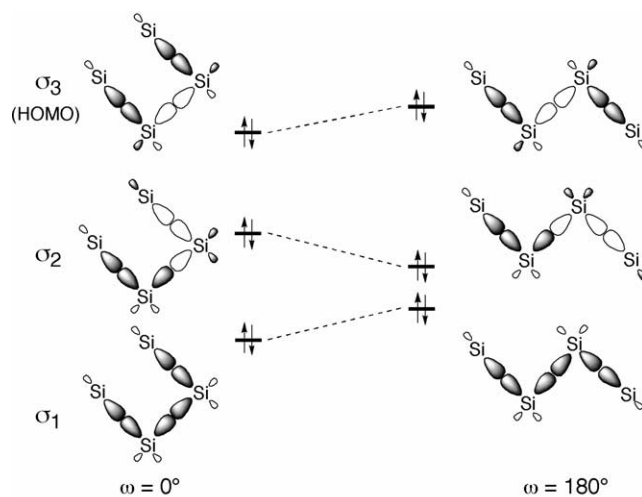

Fig. 3. Conformational dependence of three high energy occupied MOs (σ_1–σ_3) of a tetrasilane at the *syn* ($\omega = 0°$) and *anti* ($\omega = 180°$) planar limits.
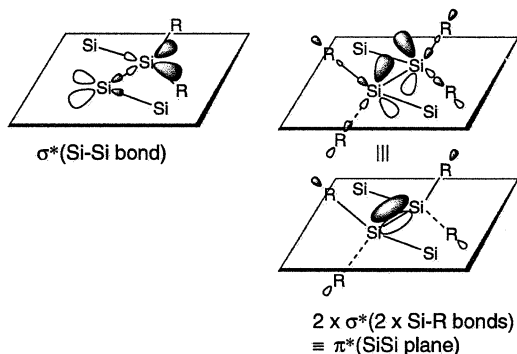
Fig. 4. MOs of the σ* (left) and π* (right) types.

3.2. Conformational effects on electronic transitions

CIS calculations on n-Si$_4$Me$_{10}$ (**1**) afford four low-lying valence excited singlet states, two of which belong to A and the others to B representation under assumption of C_2 symmetry [4]. Their excitation energies and oscillator strengths are shown in Fig. 5. We dismiss the A states from further discussion here. The σσ*-type excitation with a larger oscillator strength corresponds to the higher-energy state (2B) at $\omega = 0°$, while it corresponds to the lower-energy one (1B) at $\omega = 180°$. The opposite is the case with the σπ*-type excitation with a smaller oscillator strength. As a result of a mixing of these two types of excitations between 0 and 180° because of an avoided crossing, it is not the excitation energy but the oscillator strength of two transitions that changes dramatically as the dihedral angle changes (Fig.
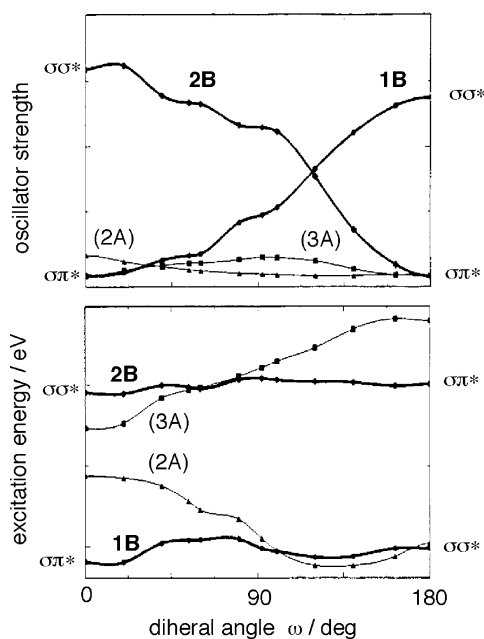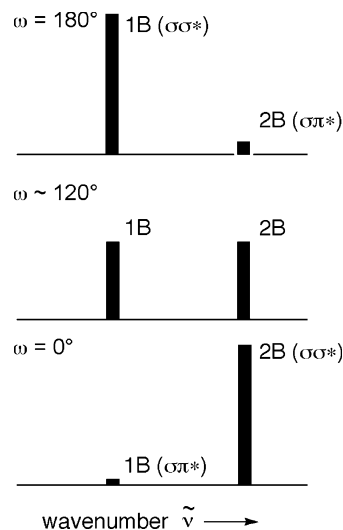

Fig. 6. Model description of the conformational dependence of two transitions of B symmetry at several dihedral angles.

6). Around $\omega = 120°$ the mixing is supposed to be the strongest and twin peaks with the same intensities can be expected; one of these will appear at a higher and the other at a lower-energy, as shown in Fig. 6B. According to higher level ab initio calculations [11,12], the situation may be even more complicated in that an additional avoided crossing probably occurs at high energies and small dihedral angles. Several experimental efforts have been carried out to confirm these predicted conformational effects on the electronic transitions of tetrasilanes.

3.3. Experimental studies

3.3.1. Matrix isolation of stable conformers of n-Si$_4$Me$_{10}$

Fig. 7A shows the conformational dependence of the potential energy of n-Si$_4$Me$_{10}$, indicating the existence of three stable conformers, i.e., gauche (G), ortho (O), and transoid (T). The UV absorption spectrum of the most stable transoid conformer was successfully separated spectrally in low temperature Ar matrices (Fig. 7B) [4]. This experiment demonstrated that the transoid conformer has an intense peak at 43 700 cm^{-1} and that the spectrally unseparated mixture of the other isomers (gauche + ortho) has a peak at 49 700 cm^{-1} as well as an absorption at 44 000–46 000 cm^{-1}. These results are fairly consistent with the expected σσ*–σπ* mixing behavior.

3.3.2. Conformational constraint by the use of cyclic structures

Cyclic structures are frequently utilized to control stereochemistry. Tetrasilanes incorporated into five- to eight-membered rings (**2–5**) were synthesized [9] to constrain the SiSiSiSi dihedral angle between 0 and 80°. Their UV absorption spectra [13,14] and dihedral angle of each compound are shown in Fig. 8. Each
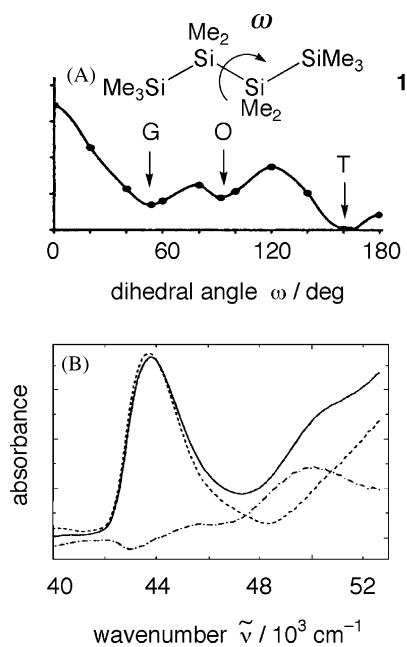

Fig. 5. Calculated oscillator strength (top) and excitation energies (bottom) of four valence transitions of n-Si$_4$Me$_{10}$ (**1**). Reprinted with permission from reference [4b]. Copyright (1996) Wiley.

Fig. 7. (A) Conformational dependence of the relative energy of *n*-Si_4Me_{10} (**1**), and (B) its matrix isolation UV absorption spectra: (—) G+O+T; (---) T; (-··-) G+O. Reproduced by permission from Willey.

compound has two transitions into B symmetry states, an intense peak at 47 800–50 400 cm^{-1} accompanied by
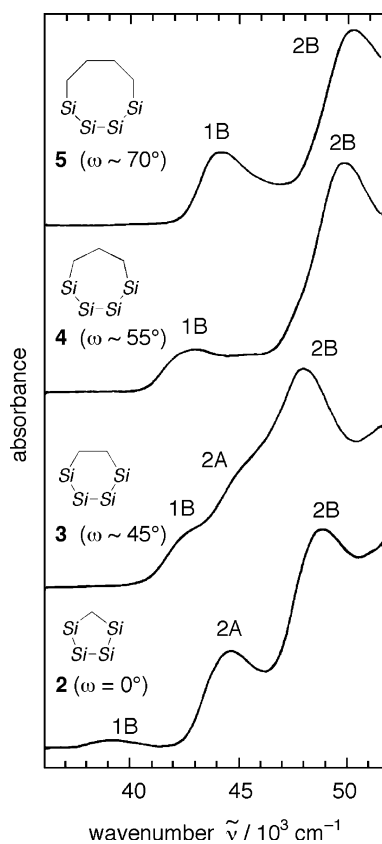

Fig. 8. UV absorption spectra of cyclic carbotetrasilanes **2**–**5**, where Si represents $SiMe_2$. Reprinted with permission from reference [13]. Copyright (1997) Elsevier.

another peak at 39 100–45 600 cm^{-1}. Tetrasilanes **2** and **3** (and indistinctly, **4**) have additional absorptions at 44 600 and 45 600 cm^{-1}, respectively. These are assigned to the 1A→2A transition, not discussed here. Although it is difficult to ascertain whether the 1A→2B transition decreases in intensity, the lower-energy transition (1A→1B) steadily becomes more intense as the dihedral angle ω increases, while their absorption maxima remain located at almost the same wavenumber except for **2**. The abnormally low excitation energy of the 1A→2B transition in **2** is attributed to the small valence angle and/or the hyperconjugation effect of the Si–C–Si moiety.

In the range of 0–80° and at ∼165°, the experiments outlined above provided quite good agreement with the calculations that suggest the avoided crossing behavior of the σσ*–σπ* mixing. However, stronger evidence is needed to complete the experimental confirmation. Especially values of the dihedral angle ω around 120° are the most crucial for the conformational effect but are missing. In this region, we can expect the strongest mixing to afford two peaks of comparable intensity, one at low and one at high energy. As seen in Fig. 7A, ω ∼ 120° corresponds to a potential energy saddle point and it seems quite difficult to produce and isolate such a conformer. Very recently, certain bicyclic systems have overcome this difficulty [14–16].

Conformationally constrained tetrasilanes **6**–**8** comprising a disilane unit with two pentamethylene tethers have been synthesized and characterized by X-ray analysis or geometry optimization calculations. Their UV absorption spectra are shown in Fig. 9 together with the dihedral angles. The tetrasilanes of *syn* (**6**) and *anti* (**8**) conformations have absorptions near 48 000 and
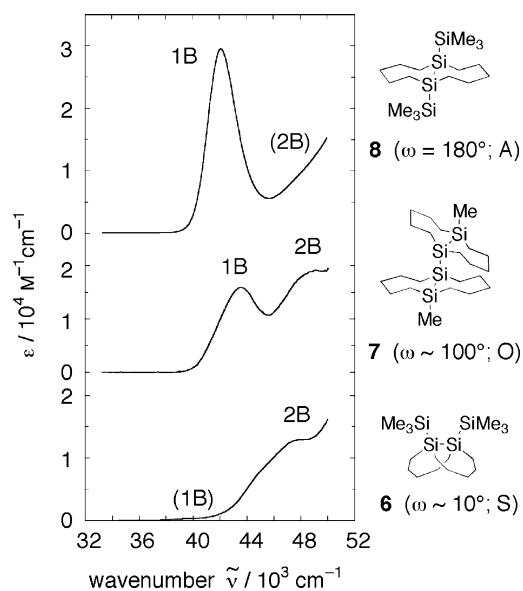

Fig. 9. UV absorption spectra of bis(pentamethylene)-tethered tetra-silanes **6**–**8**.

43 000 cm^{-1}, assignable to transitions into the 2B and 1B states, respectively. Strikingly, the *ortho*-tetrasilane (**7**) shows twin peaks whose absorption maxima are at 49 100 and 44 200 cm^{-1}, almost identical in energy with those of transitions to upper and lower B states in **6** and **8** [16]. This result fully supports the predicted $\sigma\sigma^*$–$\sigma\pi^*$ mixing, that is, two low-energy transitions into B symmetry states exchange their intensities while their excitation energies barely change.

4. Hexasilanes

Conformation control of hexasilanes has also been attained by the bicyclic disilane system and it permits a study of conformational effects [15]. The results are shown in Fig. 10. The UV absorption maximum of the *syn,anti,syn*-hexasilane **9** (SAS) appears at approximately the same wavenumber as that of the *anti*-tetrasilane (**8**), as if the two silyl groups in **9** attached at the termini in *syn*-fashion did not extend the σ-delocalized system. Replacement of one of the *syn* units of **9** with *anti* produces the *anti,anti,syn*-hexasilane **10** (AAS), whose UV absorption maximum is red-shifted by 2450 cm^{-1} (longer by 15 nm in wavelength) with a significant increase in intensity. These absorption maxima correspond to $\sigma\sigma^*$ transitions. These results demonstrate that an *anti* turn effectively extends σ-delocalization while a *syn* turn is ineffective. An attempted synthesis of all-*anti*-hexasilane did not succeed but provided the *anti,eclipsed,anti*-hexasilane **11** (AEA) instead. Its absorption maximum appears at
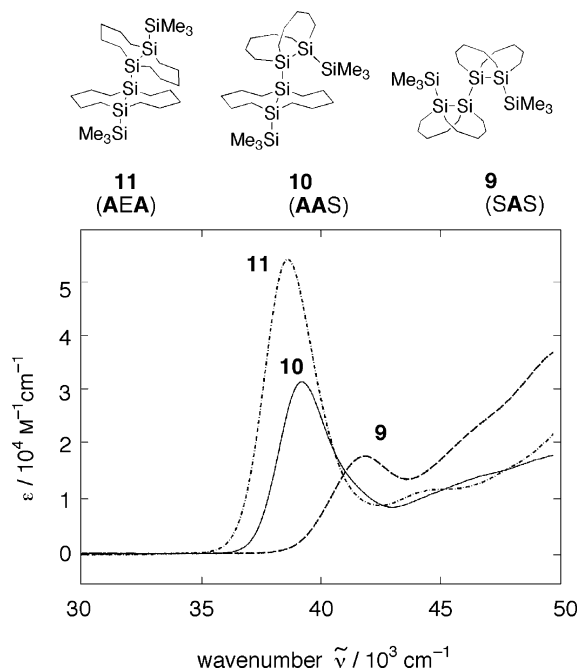
Fig. 10. UV absorption spectra of bis(pentamethylene)-tethered hexasilanes **9** (---), **10** (—), and **11** (-··-).

12 (ω = 162.5°, 178.0°, 177.4°)
λ_{max} = 37450 cm^{-1} (267 nm; ε 66800)

13 (ω = −175.70°, −167.80°, −174.30°)
λ_{max} = 37310 cm^{-1} (ε 268 nm; 33600)
(R=R'=^{n}Pr, R"=(R)-CH$_3$CH(Ph)CH$_2$-))

14 (ω = −148.08°, 173.37°, 163.90°)
λ_{max} = 37450 cm^{-1} (267 nm; ε 55600)
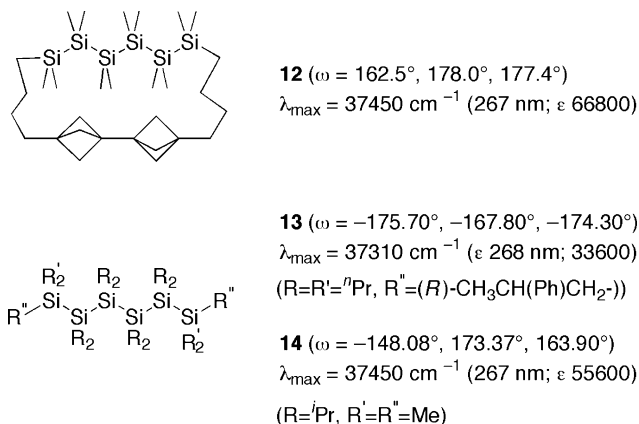
(R=^{i}Pr, R'=R"=Me)

Fig. 11. Structures and UV absorption of hexasilanes (**12–14**) with large dihedral angles.

almost the same wavenumber as that of **10**, but its extinction coefficient is much larger.

Fig. 11 summarizes the recently reported UV absorption spectral data of hexasilanes **12** [17], **13** [18], and **14** [19] whose structures were clarified by X-ray crystallography. Although their conformations are not perfectly all-*anti*, they are close to it, and their UV absorption maxima appear at 37 500–37 300 cm^{-1} (267–268 nm), red-shifted by ca. 1700 cm^{-1} ($\sim$12 nm) relative to **10**. Here we should emphasize again that σ-delocalization is effectively extended by successive SiSiSiSi fragments with large dihedral angles.

5. Summary

Recent theoretical and experimental studies of conformational effects on oligosilane photophysical properties have clarified the following facts. (1) For tetrasilanes, the strongly avoided crossing between $\sigma\sigma^*$ and $\sigma\pi^*$ configurations causes $\sigma\sigma^*$–$\sigma\pi^*$ mixing, and as a result a conformation change does not affect the excitation energies but instead affects the oscillator strengths of the two low-energy transitions into states of B symmetry. (2) For hexasilanes, it appears that the $\sigma\sigma^*$–$\sigma\pi^*$ mixing will not play a role as long as twisting occurs in a fashion that keeps the $\sigma\sigma^*$ configuration lowest in energy at all angles, and the expected redshift of the $\sigma\sigma^*$ transition then occurs as the dihedral angle grows.

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