UV Absorption and Mass Spectra of *n*-Alkylsilyl End-Capped *Anti,Cisoid*-Alternating Oligosilanes up to Docosasilane (Si_{22})

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Received November 18, 2003

Summary: We have prepared anti,cisoid-alternating oligosilanes up to Si_{22} comprising bis(tetramethylene)-tethered bicyclic disilane units end-capped with n-alkyldimethylsilyl groups to measure their UV absorption and MALDI-TOF mass spectra. It was confirmed that the absorption maximum wavelength due to the $\sigma\sigma^*$ transition remains constant in the present anti,cisoid-alternating oligosilanes irrespective of elongation of the chain length, providing the generality of the suppression effect of σ-conjugation by a cisoid turn.

Introduction

σ-Conjugated polysilanes[1] constitute an interesting class of materials and have been the subject of a large number of investigations because of their intriguing electronic properties, similar to those of the carbon π-conjugated system. One of their most important properties is their UV absorption. It is generally accepted that the absorption maximum λ_{max} red-shifts as the silicon chain becomes longer.[2] However, it was found that the UV absorption is highly dependent on the silicon backbone conformation, on the basis of the thermochromism of some polysilanes.[3] Recent theoretical and experimental studies have unveiled the conformation dependence of their photophysical properties. Due to the high and dispersed molecular weights of polysilanes, it is difficult to discuss the exact relationship between the main-chain conformation and the photophysical properties in detail.[4] Clarifying the relationship between the conformation and the electronic properties using lower members of the oligosilanes as model compounds has recently been tried, in which the conformation is controlled in a manner such as matrix isolation,[5] the utilization of cyclic[6] or bicyclic[7] structures, the introduction of bulky[8] or chiral[9,10] substituents, or inclusion into cyclodextrins.[11,12] On the basis of the UV absorption spectroscopy of these oligosilanes, it has been demonstrated that the transoid or anti conformation (SiSiSiSi dihedral angle $\omega \approx 160-180°$) effectively extends the σ conjugation, while the syn, cisoid, or gauche conformation ($\omega \approx 0-60°$) behaves as a defect.[13] Extension of the silicon chain length is highly desired in order to confirm the conformation effect on the photophysical properties of the longer oligosilanes as more precise models of the polysilanes.

So far, we have found the UV absorption maximum wavelength of the *anti,cisoid*-alternating oligosilanes comprising tetramethylene-tethered bicyclic disilane units to be almost constant, regardless of the silicon chain lengths.[7b] However, our experimental investigation of this unique behavior was limited only to relatively short oligosilanes up to decasilane Si_{10} and has essentially not yet been explored completely. In the present paper, as an extension of our recent experimental and theoretical studies, we will discuss the generality of the suppression effect of the σ conjugation by a cisoid turn on the basis of the results of the UV absorption spectra of a series of the *anti,cisoid*-alternating oligosilanes having longer chains up to docosasilane Si_{22}, the molecular weights of which were determined by MALDI-TOF mass spectroscopy.

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10.1021/om034307t CCC: $27.50
Publication on Web 02/21/2004

Scheme 1

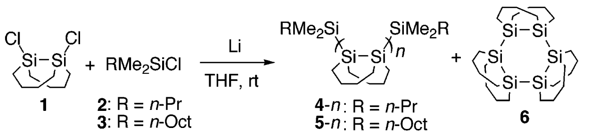

Table 1. Summary of the Wurtz-Type Reductive Coupling Reactions under Various Conditions

entry	terminator	ratio[a]	product	yield (%)[b,c] $n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
1	**2**	10/1	**4**-*n*	20	11	5.4	3.7	n.d.[d]
2		20/1		17	11	5.9	4.1	n.d.
3	**3**	1/1	**5**-*n*	35	4.3	1.4	<1	n.d.
4		10/1		34	20	7.1	2.0	n.d.
5		20/1		28	17	7.2	8.0	5.9

[a] Molar ratio of disilane **1** to terminator **2** or **3**. [b] Based on the terminator. [c] In all cases, cyclic trimer **6** was formed in 4−11% yield based on the disilane unit. [d] Not detected.

Results and Discussion

Synthesis. Synthetic results of the *anti,cisoid*-alternating oligosilanes are summarized in Scheme 1 and Table 1. The dichlorodisilane **1** was prepared as reported in the literature.[7b,14] The Wurtz-type reductive oligomerization reaction of **1** with dispersed lithium in the presence of a 0.1 mol amount of *n*-propyldimethylchlorosilane (**2**) as a terminator afforded the *n*-propyldimethylsilane end-capped *anti,cisoid*-alternating oligosilanes **4**-2 to **4**-4, in addition to the monomer **4**-1 with a cisoid conformation and the cyclic trimer **6** (entry 1). These linear and cyclic oligosilanes were separated by preparative GPC and well characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as mass spectra. No stereoisomer of each oligomer was observed, suggesting that the stereochemistry of the disilane unit was retained as observed in our previous work. The higher molecular weight oligosilanes were also produced as expected, but their solubility in various organic solvents was not improved significantly compared to the trimethylsilyl end-capped analogues.[7] As shown in entry 2, the oligomerization reaction in the ratio **1**/**2** = 20/1 effectively afforded slightly higher yields of high-molecular-weight oligomers.

To increase the solubility of the higher oligomers, we employed another longer alkyl terminator, *n*-octyldimethylchlorosilane (**3**). The reductive coupling reaction of **1** and **3** in the ratio of 1/1, 10/1, or 20/1 afforded the oligosilanes **5** and **6** (entries 3−5). The yield of the oligomers **5** varied by changing the molar ratio of **1** to **3**: an increase in the **1** to **3** ratio afforded a higher yield of the higher molecular weight oligomers. After separation of the insoluble part by filtration, the filtrate was subjected to a recycle GPC using chloroform as an eluent to separate each oligomer. Lower members of the linear oligosilanes **5**-1 to **5**-5 and the cyclic trimer **6** were separated in pure form, but a mixture of higher molecular weight oligomers was barely separated into each oligomer. Therefore, this portion was analyzed by MALDI-TOF mass spectroscopy as described below.

MALDI-TOF Mass Spectroscopy of the *Anti,Cisoid*-Alternating Oligosilanes. To the best of our knowledge, application of MALDI-TOF mass spectroscopy[15] to poly- or oligosilanes is quite rare.[16] To find the optimized conditions for the MALDI-TOF mass spectrometry system, we first tried to obtain the spectrum of the pentamer **5**-5 using 9-nitroanthracene as a matrix and silver trifluoroacetate as an additive. A good spectrum with a peak of the *m*/*z* value at 1182 corresponding to pentamer **5**-5 was obtained as shown in Figure 1. No fragmentation was observed under these conditions.

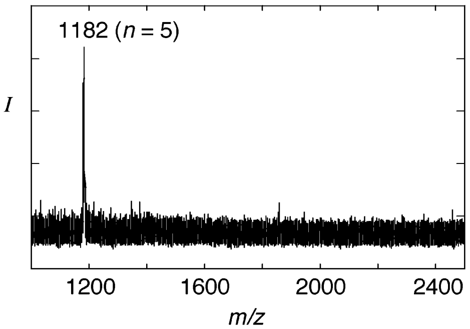

Figure 1. MALDI-TOF mass spectrum of the *n*-octylsilyl end-capped pentamer **5**-5.

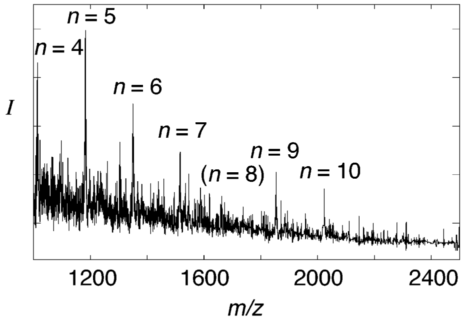

Figure 2. MALDI-TOF mass spectrum of the mixture of higher molecular weight linear oligomers **5**-*n* (*n* = 4−10).

The high-molecular-weight portion of **5** separated by preparative GPC was analyzed by MALDI-TOF mass spectroscopy under measurement conditions similar to those mentioned above, and the spectrum is shown in Figure 2. Although the signal to noise ratio is not as good as in the case of **5**-5, the existence of hexamer **5**-6, heptamer **5**-7, nonamer **5**-9, and decamer **5**-10 in addition to tetramer **5**-4 and pentamer **5**-5 is satisfactorily confirmed. However, the peak of octamer **5**-8 was barely observable due to unknown reasons.

UV Absorption Spectra of the *Anti,Cisoid*-Alternating Oligosilanes 4-*n* and 5-*n*. The UV absorption spectra of **4**-1 to **4**-4 and **5**-1 to **5**-5 were recorded at room temperature in isooctane. Only the latter spectra are shown in Figure 3, because essentially the same spectra were obtained for the former. The absorption maxima of these *anti,cisoid*-alternating oligosilanes longer than the tetrasilane remainds constant around 240 nm, similar to our previous observation, suggesting that there is little effect of the terminal alkyl chains on the photophysical properties.[7b] The first transition of the *cisoid*-tetrasilane **5**-1 appearing as a quite weak tail-like absorption around 240 nm is assignable to the $\sigma\pi^*$ excitation,[5,7] while that of other longer linear

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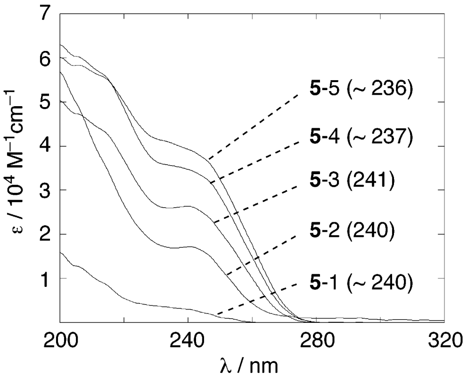

Figure 3. UV absorption spectra of the *n*-octylsilyl end-capped oligomers **5**-1 to **5**-5.

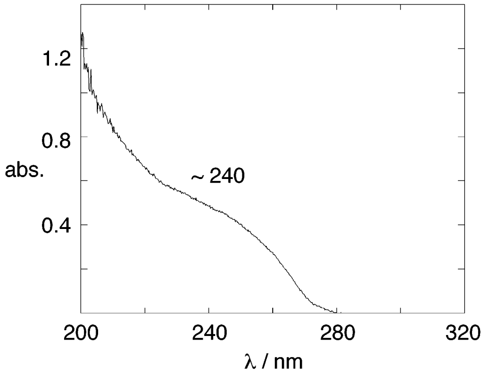

Figure 4. UV absorption spectra of a mixture of higher molecular weight linear oligomers of **5**.

oligosilanes with anti,cisoid-alternating conformations is assignable to the $\sigma\sigma^*$ excitation, mostly localized at the anti link(s).

Figure 4 shows the UV absorption spectrum of a mixture of the higher molecular weight oligosilanes of the *n*-octylsilyl end-capped oligomers **5**-*n* ($n = 4-10$), up to the Si_{22} homologues, as confirmed by MALDI-TOF mass spectroscopy. Although the spectrum no longer exhibits a clear peak, the broadened shoulder-like absorption remains around 240 nm. Interestingly, the edge of the spectrum also remains at 280 nm, regardless of the increase in the degree of oligomerization. These results provide stronger experimental support for the fact that further elongation of the silicon chain lengths does not cause any red shift in the absorption maximum because of the strongly forbidden expansion of the σ-conjugation through a cisoid turn.

Conclusion

A series of the *anti*,*cisoid*-alternating oligosilanes have been prepared by a Wurtz-type reductive coupling reaction. The oligosilanes up to the pentamer (Si_{12}) were separated by GPC, and the remaining part comprising a mixture of higher molecular weight oligosilanes up to Si_{22} homologues was analyzed to identify the components by MALDI-TOF mass spectroscopy. The UV absorption spectroscopic studies of these oligosilanes provided a strong experimental support for the fact that the σ conjugation in the *anti*,*cisoid*-alternating oligosilanes would not extend effectively through a cisoid turn.

Experimental Section

General Considerations. THF and hexane were distilled from sodium/benzophenone. Column chromatography was performed using Merck Kieselgel 60. ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300 MHz in C_6D_6. ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL EX-270 (67.80 MHz for ^{13}C and 53.54 MHz for ^{29}Si) spectrometer in C_6D_6. Chemical shifts were referenced to the internal residual solvent peak for ^1H (C_6H_6, 7.20 ppm) and ^{13}C (C_6H_6, 128.00 ppm) and to external TMS (0.00 ppm) for ^{29}Si. Recycle preparative gel permeation chromatography (GPC) was performed using polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with chloroform as an eluent. MALDI-TOF mass spectra were recorded on an Applied Biosystems Voyager-DE STR mass spectrometer in a linear mode. UV absorption spectra were recorded on a Shimadzu UV-PC 3101 spectrophotometer in either isooctane or 3-methylpentane at room temperature.

Wurtz-Type Reductive Oligomerization. Typical Procedure. To a suspension of Li (0.25 g, 36 mmol; 30% dispersion in mineral oil, washed prior to use with hexane followed by THF) in THF (4.0 mL) was added a mixture of **1**[7c] (1.1 g, 4.5 mmol) and *n*-propyldimethylchlorosilane (**2**; 0.23 mmol) in THF (2.0 mL) over a period of 5 min at 0 °C under an Ar atmosphere, and the reaction mixture was stirred for 1 day at ambient temperature. After being quenched with 2-propanol followed by water, the resulting mixture was extracted with toluene. The combined organic layer was washed with brine, dried over $MgSO_4$, and filtered, and the solution was concentrated under reduced pressure. The resulting crude product was passed through a short-path column (SiO_2) using toluene as an eluent to give a mixture of oligosilanes **4**-1 to **4**-4 and the cyclic trimer **6**. Oligosilanes **4**-1 to **4**-4 and **6** were separated by GPC using chloroform as an eluent.

In this section, the *n*-propyldimethylsilyl and *n*-octyldimethylsilyl groups and the *cisoid*-disilane unit are abbreviated PDS, ODS, and *C*-Si_2, respectively, and thus **4** and **5** are described as PDS-[*C*-Si_2]$_n$-PDS (**4**-*n*) and ODS-[*C*-Si_2]$_n$-ODS (**5**-*n*), respectively.

PDS-[*C*-Si_2]-PDS (4-1). Colorless liquid. ^1H NMR: δ 0.26 (s, 12H), 0.76 (m 4H), 0.88−1.02 (m, 8H), 1.08 (t, $J = 7.2$ Hz, 6H), 1.40−1.52 (m, 4H), 1.62−1.88 (m, 8H). ^{13}C NMR: δ −2.36, 11.27, 18.79, 18.92, 19.08, 26.90. ^{29}Si NMR: δ −50.60, −15.28. MS (EI; *m*/*z* (relative intensity)): 370 (M^+, 100), 269 ([M − *n*-$PrMe_2Si$]$^+$, 43). Anal. Calcd for $C_{18}H_{42}Si_4$: C, 58.29; H, 11.41. Found: C, 58.25; H, 11.55. UV absorption: λ_{max} ~240 nm ($\epsilon = 4.2 \times 10^3$).

PDS-[*C*-Si_2]$_2$-PDS (4-2). White waxy solid. ^1H NMR: δ 0.27 (s, 12H), 0.77 (m, 4H), 0.89−1.24 (m, 22H), 1.40−1.52 (m, 4H), 1.62−1.90 (m, 16H). ^{13}C NMR: δ −2.28, 11.53, 12.99, 18.77, 18.94, 19.05, 26.80, 26.92. ^{29}Si NMR: δ −49.67, −45.86, −15.05. MS (EI; *m*/*z* (relative intensity)): 538 (M^+, 100). Anal. Calcd for $C_{26}H_{58}Si_6$: C, 57.91; H, 10.84. Found: C, 57.68; H, 10.98. UV absorption: λ_{max} 240 nm ($\epsilon = 1.7 \times 10^4$).

PDS-[*C*-Si_2]$_3$-PDS (4-3). White waxy solid. ^1H NMR: δ 0.28 (s, 12H), 0.78 (m, 4H), 0.89−1.29 (m, 30H), 1.42−1.52 (m, 4H), 1.62−2.12 (m, 24H). ^{13}C NMR: δ −2.29, 11.58, 13.13, 13.34, 18.77, 18.94, 19.05, 26.82, 26.93, 27.01. ^{29}Si NMR: δ −49.59, −45.31, −44.86, −14.38. MS (EI; *m*/*z* (relative intensity)): 706 (M^+, 100). Anal. Calcd for $C_{34}H_{74}Si_8$: C, 57.71; H, 10.54. Found: C, 58.04; H, 10.71. UV absorption: λ_{max} 240 nm ($\epsilon = 2.8 \times 10^4$).

PDS-[*C*-Si_2]$_4$-PDS (4-4). White waxy solid. ^1H NMR: δ 0.28 (s, 12H), 0.78 (m, 4H), 0.9−1.32 (m, 38H), 1.41−1.52 (m, 4H), 1.62−2.06 (m, 32H). ^{13}C NMR: δ −2.29, 11.58, 13.13, 13.40, 13.46, 18.77, 18.95, 19.05, 26.82, 28.83, 26.93, 26.95. ^{29}Si NMR: δ −49.72, −45.34, −45.04, −44.51, −14.98. MS (FAB; *m*/*z* (relative intensity)): 874 (M^+, 22). HRMS: calcd for $C_{34}H_{74}Si_8$, 874.4735; found, 874.4747. UV absorption: λ_{max} 236 nm ($\epsilon = 3.6 \times 10^4$).

ODS-[*C*-Si$_2$]-ODS (5-1). Colorless liquid. ^{1}H NMR: δ 0.31 (s, 12H), 0.84 (t, J = 9.6, 6.0 Hz, 4H), 0.92−1.12 (m, 14H), 1.32−1.58 (m, 24H), 1.64−1.94 (m, 8H). ^{13}C NMR: δ −2.34, 11.28, 14.53, 16.48, 23.28, 25.34, 26.92, 29.94, 29.98, 32.49, 34.45. ^{29}Si NMR: δ −50.62, −14.88. MS (EI; m/z (relative intensity)): 510 (M$^+$, 100), 339 ([M − n-OctMe$_2$Si]$^+$, 9.1). HRMS: calcd for $C_{28}H_{62}Si_4$, 510.3929; found, 510.3921. UV absorption: λ_{max} ~240 nm ($\epsilon = 3.0 \times 10^3$).

ODS-[*C*-Si$_2$]$_2$-ODS (5-2). White waxy solid. ^{1}H NMR: δ 0.31 (s, 12H), 0.84 (t, J = 9.6, 6.0 Hz, 4H), 0.92−1.08 (m, 14H), 1.09−1.30 (m, 8H), 1.31−1.58 (m, 24H), 1.66−1.98 (m, 16H). ^{13}C NMR: δ −2.28, 11.60, 13.06, 14.53, 16.47, 23.28, 25.30, 26.83, 26.97, 29.94, 29.96, 32.51, 34.44. ^{29}Si NMR: δ −49.69, −45.79, −14.68. MS (EI; m/z (relative intensity)): 678 (M$^+$, 100). HRMS: calcd for $C_{36}H_{78}Si_6$, 678.4719; found, 678.4725. UV absorption: λ_{max} 240 nm ($\epsilon = 1.7 \times 10^4$).

ODS-[*C*-Si$_2$]$_3$-ODS (5-3). White waxy solid. ^{1}H NMR: δ 0.31 (s, 12H), 0.85 (t, J = 9.9, 5.7 Hz, 4H), 0.91−1.08 (m, 14H), 1.09−1.30 (m, 16H), 1.32−1.56 (m, 24H), 1.65−2.00 (m, 24H). ^{13}C NMR: δ −2.29, 11.65, 13.16, 13.41, 14.53, 16.45, 23.28, 25.29, 26.83, 26.87, 26.95, 29.93, 29.94, 32.51, 34.44. ^{29}Si NMR: δ −49.74, −45.39, −44.93, −14.60. MS (FAB; m/z (relative intensity)): 846 (M$^+$, 100). HRMS: calcd for $C_{44}H_{94}Si_8$, 846.5510; found, 846.5535. UV absorption: λ_{max} 241 nm ($\epsilon = 2.6 \times 10^4$).

ODS-[*C*-Si$_2$]$_4$-ODS (5-4). White waxy solid. ^{1}H NMR: δ 0.31 (s, 12H), 0.85 (t, J = 10.2, 6.0 Hz, 4H), 0.92−1.08 (m, 14H), 1.10−1.30 (m, 24H), 1.31−1.58 (m, 24H), 1.66−2.04 (m, 32H). ^{13}C NMR: δ −2.31, 11.61, 13.13, 13.14, 13.46, 14.54, 16.43, 23.28, 25.29, 26.85, 26.88, 26.90, 26.95, 29.93, 29.94, 32.51, 34.44. ^{29}Si NMR: δ −49.74, −45.28, −45.01, −44.48, −14.60. MS (FAB; m/z (relative intensity)): 1014 (M$^+$, 4.1). HRMS: calcd for $C_{52}H_{110}Si_{10}$, 1014.6300; found, 1014.6270. UV absorption: λ_{max} ~237 nm ($\epsilon = 3.5 \times 10^4$).

ODS-[*C*-Si$_2$]$_5$-ODS (5-5). White waxy solid. ^{1}H NMR: δ 0.32 (s, 12H), 0.85 (t, J = 9.6, 6.3 Hz, 4H), 0.92−1.09 (m, 14H), 1.10−1.32 (m, 32H), 1.32−1.57 (m, 24H), 1.68−2.04 (m, 40H). ^{13}C NMR: δ −2.31, 11.63, 13.14, 13.47, 13.52, 13.54, 14.54, 16.43, 23.28, 25.30, 26.85, 26.88, 26.90, 26.93, 26.95, 29.93, 29.94, 32.51, 34.44. ^{29}Si NMR: δ −49.74, −45.26, −45.04, −44.56, −44.36, −14.60. MS (FAB; m/z) 1182 (M$^+$). UV absorption: λ_{max} ~236 nm ($\epsilon = 4.0 \times 10^4$).

MALDI-TOF Mass Measurements. The MALDI-TOF system was calibrated with angiotensin I at 10 μM in combination with the matrix (α-cyano-4-hydroxycinnamic acid) as a standard. All samples were prepared according to the procedure of Jones et al.[16] described as follows: equal quantities of the matrix (9-nitroanthracene) and the oligosilane solution (0.1 M) were mixed, and then 1.0 μL of this mixture was deposited as a drop on 1.0 μL of the aqueous silver trifluoroacetate solution (0.1 M) on the target plate. Rapid mixing of the organic and aqueous layers was observed, and the irregular precipitation of the matrix−analyte−salt mixture was obtained.

The spectra were recorded using the sample so obtained. The observed peaks in Figure 2 are listed as follows: 1013 (n = 4), 1182 (n = 5), 1350 (n = 6), 1517 (n = 7), 1854 (n = 9), and 2023 (n = 10). Although there are some discrepancies between the observed and actual molecular weights, the degree is within experimental error.

Acknowledgment. We thank Prof. Richard G. Jones, University of Kent, for kindly providing the experimental details of the MALDI-TOF mass spectroscopy of oligosilanes, as a part of the dissertation of his co-worker Dr. William K. C. Wong. Without their pioneering results, our work would not be possible. We are grateful that Prof. Jones has agreed for us to publish our results prior to their publication. Financial support by the Ministry of Education, Culture, Sports, Science, and Technology of Japan for a Grant-in-Aid for COE Research on Elements Science (No. 12CE2005) is acknowledged.

OM034307T