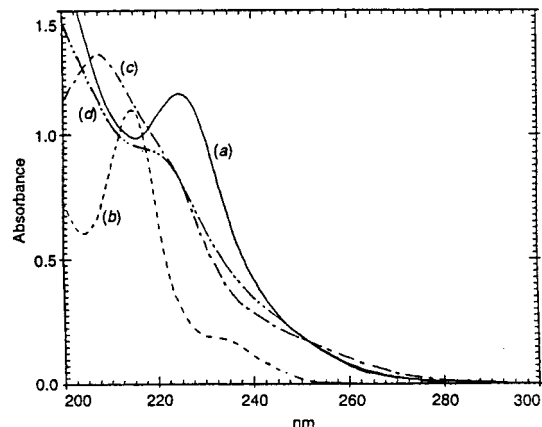


**Figure 1.** X-ray structures of **3** and **4**. Selected bond distances (Å) and angles (deg). **3**: Si1–Si2 = 2.329(1), Si1–O1 = 1.947(2), Si1–Cl1 = 2.367(1), Si1–C1 = 1.903(3); Si2–Si1–Si3 = 122.73(4), Si2–Si1–C1 = 122.1(1), Si3–Si1–C1 = 115.1(1), Cl1–Si1–O1 = 170.70(6). **4**: Si1–Si3 = 2.3395(6), Si1–Si2 = 2.3362(5), Si2–Si4 = 2.3447(7), Si1–Cl1 = 2.3217(6), Si1–O1 = 1.981(1), Si2–Cl2 = 2.3704(5), Si2–O2 = 1.943(1); C1–Si1–Si2 = 116.96(5), C1–Si1–Si3 = 123.03(5), Si2–Si1–Si3 = 119.09(2), Cl1–Si1–O1 = 172.03(4), C5–Si2–Si4 = 117.30(6), Si1–Si2–Si4 = 126.27(2), Si1–Si2–C5 = 116.41(6), Cl2–Si2–O2 = 172.49(4).



**Figure 2.** UV spectra of (a) **3**, (b) 2-chloroheptamethyltrisilane, (c) **4** in isoctane solution, and (d) **4** in acetonitrile solution.

two equatorial methyl groups in **5** by two silyl groups has no influence on the strength of the O–Si bond.<sup>16</sup> This result is somewhat surprising, because the presence of an electropositive ligand such as silicon in the equatorial position is supposed to weaken the coordination bond.<sup>3,7c</sup>

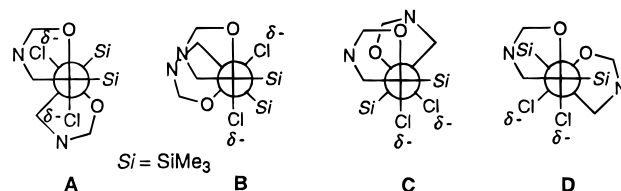
The UV spectra of **3** and **4** are shown in Figure 2, in which the spectrum of 2-chloroheptamethyltrisilane is also given for comparison. In isoctane solution, **3** exhibited a strong absorption at 227 nm ((a),  $\epsilon = 7045 \text{ cm}^{-1} \text{ M}^{-1}$ ), which can be assigned to  $\sigma \rightarrow \sigma^*$  transition of the Si–Si bond.<sup>1a,17</sup> It should be noted that the absorption maximum of **3** appears at the longest wavelength among various  $\text{Me}_3\text{SiSi}(X)\text{MeSiMe}_3$  ( $X = \text{halogen, N, O, S, Me}$ ).<sup>17</sup> For example, compared with the spectrum of  $(\text{Me}_3\text{Si})_2\text{Si}(\text{Cl})\text{CH}_3$  ((b),  $\lambda_{\text{max}} = 215 \text{ nm}$ ,  $\epsilon = 7300 \text{ cm}^{-1} \text{ M}^{-1}$ ), the  $\lambda_{\text{max}}$  of **3** is red-shifted by 12 nm. The strong bathochromic shift is apparently a result of an electronic perturbation of the Si–Si bond by the pentacoordinate moiety. To gain an insight of this point, *ab initio* calculations (CIS/6-31G\*\*) were carried out on model

compounds,  $(\text{H}_3\text{Si})_2\text{Si}(\text{Cl})\text{CH}_2\text{NHCHO}$  **6** and  $(\text{H}_3\text{Si})_2\text{Si}(\text{Cl})\text{CH}_3$  **7**, where the structures were optimized at the B3LYP/6-31G\*\* level.<sup>18</sup> The calculated  $\lambda_{\text{max}}$  of **6** was red-shifted by 6.2 nm from

(16) The strength of the O–Si coordination bond is reflected in the shift of the  $\nu(\text{CO})$ : Macharashvili, A. A.; Shklover, V. E.; Chernikova, N. Yu.; Antipin, M. Yu.; Struchkov, Yu. T.; Baukov, Yu. I.; Oleneva, G. I.; Kramarova, E. P.; Shipov, A. G. *J. Organomet. Chem.* **1989**, 359, 13.

(17) Pitt, C. G. *J. Am. Chem. Soc.* **1969**, 91, 6613.

## Scheme 2



that of **7**, and the strongest absorption was mainly originated by the  $\sigma_{\text{SiSi}} \rightarrow \sigma^*_{\text{SiSi}}$  transition in both molecules. Compared with the corresponding orbitals of **7**, the  $\sigma_{\text{SiSi}}$  orbital of **6** is substantially destabilized, whereas the  $\sigma^*_{\text{SiSi}}$  orbital of **6** is slightly destabilized. The lone pair orbital on oxygen shifts up the  $\sigma_{\text{SiSi}}$  orbital of **6** in energy, while it does not affect the  $\sigma^*_{\text{SiSi}}$  orbital of the different symmetry. Thus, the red shift in the absorption spectra of **6** is theoretically explained as the result of an interaction between the oxygen lone pair orbital and the  $\sigma_{\text{SiSi}}$  orbital.

In striking contrast, the  $\lambda_{\text{max}}$  of **4** ((c), 207 nm,  $\epsilon = 8400 \text{ cm}^{-1} \text{ M}^{-1}$  in isoctane) appeared at the shorter-wavelength region relative to **3**, although the presence of the two pentacoordinate silicon moieties are expected to be more effective in destabilizing the  $\sigma_{\text{SiSi}}$ . We attribute this unusual spectral property of **4** primarily to a conformational effect on the electronic structure. Recent studies on conformationally constrained tetrasilanes have clearly demonstrated that pseudo-gauche conformation (the Si–Si–Si dihedral angle ( $\omega$ ) = 55°) causes a significant decrease of absorbance in the longer-wavelength region above 220 nm.<sup>19</sup> As suggested by the crystal structure of **4** ( $\omega = 57.14(4)^\circ$ ), the lowest energy conformation of **4** in solution seems to be gauche-like (conformer **A** in Scheme 2);<sup>20</sup> this conformation would be responsible for the disappearance of the absorption in the longer-wavelength region. Our hypothesis is strengthened by the observation that the UV spectrum of **4** displayed a solvent-sensitive red shift of the  $\lambda_{\text{max}}$  in acetonitrile solution (Figure 2d), suggesting that greater contribution of other conformer like **D** in polar solvent gave rise to the observed red shift.<sup>21</sup> However, at the present stage, it is difficult to separate the inherent electronic effects of the two pentacoordinate silicon moieties on the electronic structure of **4** from the conformational effects; further study is needed to clarify this point.

Currently, we are studying the electronic properties of various types of hexa- and pentacoordinate oligosilanes as well as the synthesis of pentacoordinate polysilanes with high molecular weights.

**Acknowledgment.** We are grateful to Professor Keiji Morokuma, Emory University, for helpful discussion and to the Japan Science and Technology Corporation (JST) for financial support through the CREST (Core Research for Evolution Science and Technology) program and for a postdoctoral fellowship to I.E.-S.

**Supporting Information Available:** Experimental details and characterization data for all new compounds, including tables of crystal data, atomic coordinates, bond distances, and angles for **3** and **4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA982943Q

(18) Detailed accounts of the calculated structures and the energies will be reported elsewhere. All calculations were carried out using the program Gaussian 94, Revision E.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(19) (a) Plitt, H. S.; Michl, J. *Chem. Phys. Lett.* **1992**, 198, 400. (b) Imhof, R.; Teramae, H.; Michl, J. *Chem. Phys. Lett.* **1997**, 270, 500.

(20) Other conformers depicted in Scheme 2 seem to be less stable, due to the steric repulsion between the neighboring rings (conformer **B**) or an enhanced dipole moment derived from the highly polarized Si–Cl bonds (conformers **C** and **D**).

(21) Oka, K.; Fujiiue, N.; Dohmaru, T.; Yuan, C.-H.; West, R. *J. Am. Chem. Soc.* **1997**, 119, 4074.