Synthesis and Mesomorphic Properties of 1,10-Dialkylpermethyldecasilanes

Tetsuo Yatabe,* Takeshi Kanaiwa,† Hideki Sakurai,† Hajime Okumoto, Akira Kaito, and Yoshikazu Tanabe
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305
†*Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo,*
2641 Yamazaki, Noda, Chiba 278

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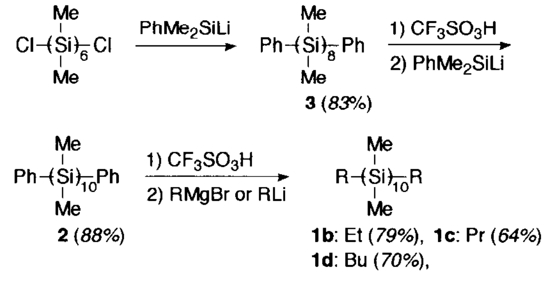
Decasilanes, $R(SiMe_2)_{10}R$ where R = Et, Pr, and Bu, show the enantiotropic mesophase with a multilayer interdigitated structure. In the mesophase, the silicon chains adopt an almost all-*trans* conformation, and the decasilanes show absorption bands with maxima at 293 (R = Et) and 294 nm (R = Pr and Bu).

Linear oligosilanes have attracted much interest because of their unique electronic and optical properties, particularly electronic absorption and fluorescence.[1,2a] These physical properties are attributed to the σ-electron delocalization along the silicon main chain,[1,3] and thus anisotropic with respect to the silicon chain direction.[2a] In order to investigate the essence of the physical properties, molecularly oriented solids (*e.g.* a vacuum-deposited film[2a] and a single crystal[1d]) and liquid crystals[2b,c] are indispensable. Very recently, we have reported liquid crystalline behavior of permethyloligosilanes, $Me(SiMe_2)_nMe$ where n = 9, 10 (**1a**), 11, and 12.[2c] These oligosilanes show the smectic B phase, where the oligosilane molecules are hexagonally ordered within the smectic layer unlike fluid nematic and smectic A phases. Therefore, their oligosilane derivatives would be suitable to understand the relationship between the conformations and the electronic properties. In addition, these oligosilane liquid crystals are very interesting as a new class of materials such as liquid crystalline photoconductors.[4] Decasilane derivatives with alkyl chains at the both ends of the oligosilane unit are expected to show a mesophase around room temperature, because **1a** forms the mesophase from 82 to 114 °C on heating and from 111 to 74 °C on cooling.[2c] Herein, we report the synthesis and mesomorphism of a series of 1,10-dialkylpermethyldecasilanes, $R(SiMe_2)_{10}R$ where R = Et, Pr, and Bu, together with their conformations and UV absorption spectra in the mesophase.

Decasilanes **1b-d** were synthesized in a three-step reaction as shown in Scheme 1.[5,6] A THF solution of $PhMe_2SiLi$ was added to 1,6-dichloropermethylhexasilane in hexane, giving 1,8-diphenylpermethyloctasilane (**3**) in 83% yield. Treatment of **3** with CF_3SO_3H, followed by addition of $PhMe_2SiLi$ gave 1,10-diphenylpermethyldecasilane (**2**) in 88% yield. 1,10-Bis(trifluoromethanesulfonyl)decasilane derived from **2** was allowed to react with Grignard reagents or alkyllithiums to obtain **1b-d** as a white waxy solid in a moderate yield, respectively.



Scheme 1.

The thermal properties of decasilanes **1b-d** were examined by the combination of DSC measurements and polarizing microscopy. The values for the transition temperatures and the associated enthalpies for these compounds are summarized in Table 1. For all the compounds a texture similar to a lancet texture typical of a smectic B phase[2c,7] was observed both on cooling and on heating, indicating that these decasilanes show the enantiotropic mesophase. Decasilane **1b** has the mesomorphic state in the range of 50-105 °C on heating and 106-49 °C on cooling. Decasilane **1c** forms the mesophase from 22 to 87 °C on heating and from 86 to 21 °C on cooling, and another mesophase or a crystalline phase (X phase) from 21 to 12 °C on cooling. Decasilane **1d**, like **1c**, forms the mesophase on heating (23-69 °C) and both the mesophase and the X phase on cooling (69-18-13 °C). Although the isotropization temperatures decrease monotonously from 105 to 69 °C with increasing length of the alkyl chains at the both ends of the decasilane unit, the mesomorphic ranges are wider than that for **1a**, and **1c** and **1d** form the mesophase at room temperature on cooling.

Furthermore, the molecular alignment for decasilanes **1b-d** in the mesophase were investigated by X-ray diffraction method. The *d*-spacings are listed in Table 2. These decasilanes show the X-ray diffraction pattern very similar to that observed for **1a**, except for the layer spacings. The intermolecular distances between the nearest molecules (the hexagonal lattice constant $a = d_{100} \times 2/\sqrt{3}$: 7.85, 7.78, and 7.78 Å for **1b**, **1c**, and **1d**, respectively) are very close to that for **1a** (7.91 Å).[2c] Although the extended molecule of **1b** is longer by 2.5 Å than that of **1a**, as estimated from a molecular model, the layer spacing for **1b** (d_{002} = 21.9 Å) is slightly larger than that for **1a** (21.5 Å). The layer spacings increase regularly by 1.2-1.3 Å per methylene with increasing length of the alkyl chain (23.2 and 24.4 Å for **1c**

Table 1. Transition temperatures and enthalpies (Δ*H*) for 1,10-dialkylpermethyldecasilanes **1b-d**, $R(SiMe_2)_{10}R$

compd	R	transition temperatures / °C [Δ*H* / kJmol⁻¹][a]
1b	Et	$\mathrm{K} \underset{49\,[11.7]}{\overset{50\,[11.9]}{\rightleftarrows}} \mathrm{M} \underset{106\,[14.0]}{\overset{105\,[14.1]}{\rightleftarrows}} \mathrm{I}$
1c	Pr	$\mathrm{K} \xrightarrow{22\,[22.1]} \mathrm{M} \underset{86\,[13.7]}{\overset{87\,[14.2]}{\rightleftarrows}} \mathrm{I}$ $\mathrm{M} \xrightarrow{21\,[17.4]} \mathrm{X} \xrightarrow{12\,[3.4]} \mathrm{K}$
1d	Bu	$\mathrm{K} \xrightarrow{23\,[28.6]} \mathrm{M} \underset{69\,[12.4]}{\overset{69\,[12.5]}{\rightleftarrows}} \mathrm{I}$ $\mathrm{M} \xrightarrow{18\,[20.6]} \mathrm{X} \xrightarrow{13\,[7.1]} \mathrm{K}$

[a] K: crystalline, X: crystalline or mesophase, M: mesophase, I: isotropic.

Table 2. The *d*-spacings / Å and the lattice constant *a* / Å for 1,10-dialkylpermethyldecasilanes **1b-d** in the mesophase

compd	d_{002}	Δd_{002}	d_{004}	d_{100}	d_{110}	a
1b	21.9	1.3	11.0	6.80	3.96	7.85
1c	23.2	1.2	11.6	6.74	3.93	7.78
1d	24.4		12.2	6.74	3.92	7.78

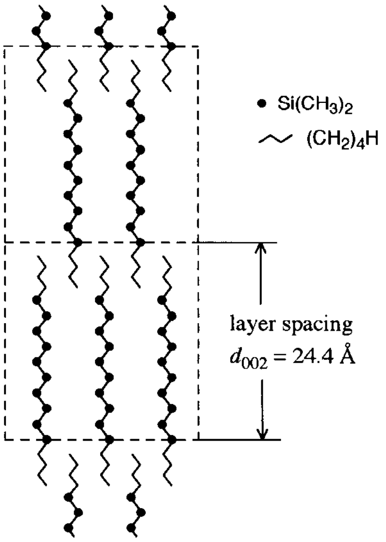


Figure 1. Schematic illustration of the multilayer interdigitated structure for decasilane **1d** in the mesophase.

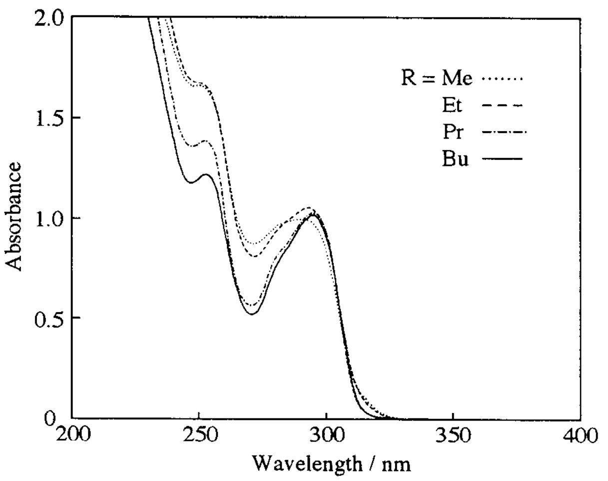


Figure 2. UV absorption spectra of 1,10-dialkylpermethyldecasilanes **1a-d**, $R(SiMe_2)_{10}R$, in the mesophase.

and **1d**, respectively). In addition, these spacings are in good agreement with the values calculated by use of the equation: $9d_{SiSi} + 2d_{SiC} + (n-1)d_{CC}$, where n is the number of carbon atoms in the alkyl chain and d_{XY} is the spacing between atoms X and Y in the direction of molecular chain with an all-*trans* conformation: d_{SiSi} = 1.99; d_{SiC} = 1.53; d_{CC} = 1.24 Å, estimated from a molecular model. These results indicate that the oligosilane molecules are hexagonally ordered to form a multilayer interdigitated structure, and that the alkyl and silicon chains adopt almost all-*trans* conformations and are perpendicular to the layers, as illustrated in Figure 1.

The UV absorption spectra of the decasilanes in the mesophase are of particular interest. Absorption bands with maxima at 292 (ε = 1700), 293 (ε = 2000), 294 (ε = 1900), and 294 nm (ε = 2200) are observed for **1a-d** in the mesophase, respectively (Figure 2).[8] These absorption bands are red-shifted by 12-14 nm and the molar extinction coefficients are very small, as compared to those in the liquid state (λ_{max} = 279-280 nm, ε = 25000-28000) and in solution (λ_{max} = 280-281 nm, ε = 40900-41400).[8] The red-shifts observed in the mosophase can be interpreted in terms of the conformation of the silicon chain, which affects the electronic absorption. In solution and in the liquid state, the dihedral angles for the silicon tetrads should be in the range of 165-170 deg (an approximately 15/7 helix conformation).[1a-d] The conformation in the mesophase is closer to an all-*trans* conformation than those in solution and in the liquid state, being stabilized by the intermolecular interactions in the hexagonal packing and the interdigitated structure. In addition, the absorption band for **1b** in the mesophase is somewhat broader than those for **1c** and **1d** and similar to that for **1a**, indicating that the interdigitated interactions between the alkyl chains in **1b** are weaker than those in **1c** and **1d**.

References and Notes

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5 Decasilanes **1b-d** were successfully purified with a preparative HPLC. The spectral data for **1d** were descrived as a representative. **1d**: ^1H NMR ($CDCl_3$, δ) 0.05 (s, 12 H), 0.13 (s, 12 H), 0.17 (s, 12 H), 0.190 (s, 12 H), 0.194 (s, 12 H), 0.60 (t, J = 8.0 Hz, 4 H), 0.87 (t, J = 6.8 Hz, 6 H), 1.18-1.39 (m, 8 H); ^{13}C NMR ($CDCl_3$, δ) -5.17, -4.20, -3.97, -3.16, 13.8, 15.5, 26.7, 26.8.

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8 The molar extinction coefficients ($Lmol^{-1}cm^{-1}$) in the mesophase and in the liquid state were given by applying Lambert-Beer's law, like solution. Decasilanes **1a-d** show absorption maxima at 279 (ε = 26000), 280 (ε = 26000), 280 (ε = 28000), and 280 nm (ε = 25000) in the liquid state, respectively. In solution, absorption bands with maxima at 280 (ε = 40900), 281 (ε = 41400), 281 (ε = 41000), and 281 nm (ε = 41100) are observed for **1a-d**, respectively.