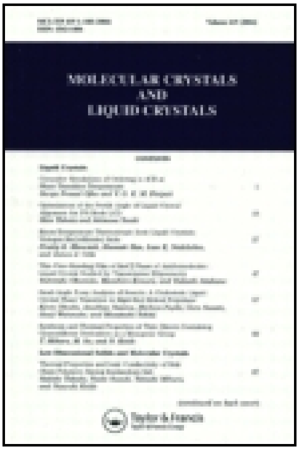

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis and Mesomorphism of 1,10-Dialkylpermethyl-Decasilanes

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Synthesis and Mesomorphism of 1,10-Dialkylpermethyl-Decasilanes

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1,10-dialkylpermethyldecasilanes, $R[Si(CH_3)_2]_{10}R$ where $R = C_2H_5$ (**1b**), C_3H_7 (**1c**), and C_4H_9 (**1d**), were prepared from 1,6-dichloropermethylhexasilane in a three-step reaction. Decasilanes **1b-d** show the enantiotropic mesophase in the range of 50–105, 22–87, and 23–69 °C, respectively. The molecular alignment for the decasilanes in the mesophase were investigated by X-ray diffraction method. These oligosilane molecules are hexagonally ordered to form a multilayer interdigitated structure. The alkyl and silicon chains of these oligosilanes adopt almost all-*trans* conformations and are perpendicular to the layers. These decasilanes show absorption bands with maxima at 293–294 nm in the mesophase. These absorption maxima are red-shifted by 12–14 nm, comparing with those in the liquid state and in solution.

Keywords: oligosilanes; decasilanes; mesophase; interdigitated structure; electronic absorption

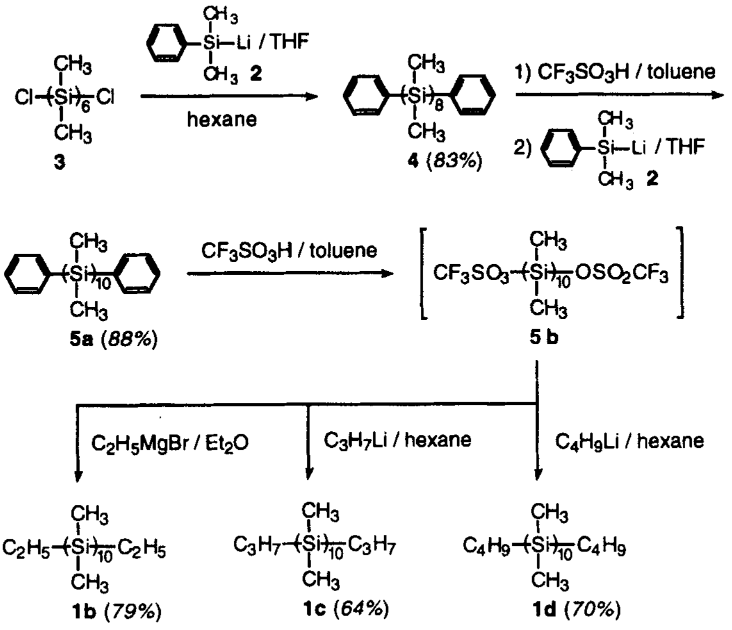
INTRODUCTION

Linear oligosilanes, $R(SiR_2)_nR$ where n = 4-20, have attracted much interest due to their unique electronic and optical properties, particularly electronic absorption and fluorescence[1]. These physical properties are attributed to the σ-electron delocalization along the silicon main chain, and thus affected by the conformation of the silicon chain and anisotropic with respect to the silicon chain direction[2,3a]. Liquid crystalline oligosilanes are very interesting as a new class of materials because the physical properties in the liquid crystalline phase are expected to be different from those in solution and in the liquid and solid phases[3]. In addition, the physical properties would be anisotropically controlled by the application of magnetic and electric fields in the liquid crystalline state. Very recently, we have reported liquid crystalline behavior of permethyloligosilanes, $CH_3[Si(CH_3)_2]_nCH_3$ where n = 9, 10 (**1a**), 11, and 12[3c,d], which have no mesogenic units such biphenyl groups and no flexible units such as alkyl chains. These oligosilanes show the enantiotropic smectic B phase. In the mesophase, the oligosilane molecules are hexagonally ordered within the smectic layer unlike fluid nematic and smectic A phases, and the silicon chains adopt an almost all-*trans* conformation. Therefore, their oligosilane derivatives would be suitable to understand the relationship between the conformations and the electronic properties. Decasilane derivatives with alkyl chains at the both ends of the oligosilane unit, $R[Si(CH_3)_2]_{10}R$, are expected to show a mesophase around room temperature, because decasilane **1a** forms the mesophase in the range of 82-114 °C on heating and 111-74 °C on cooling. Herein, we report the synthesis and mesomorphism of a series of 1,10-dialkylpermethyldecasilanes, $R[Si(CH_3)_2]_{10}R$ where R = C_2H_5 (**1b**), C_3H_7 (**1c**), and C_4H_9 (**1d**), together with their conformations and electronic absorption spectra in the mesophase.

RESULTS AND DISCUSSION

Synthesis

1,10-Dialkylpermethyldecasilanes (**1b**-**d**) were synthesized in a three-step reaction as shown in Scheme 1. A solution of (dimethylphenylsilyl)lithium (**2**) in THF was added dropwise to a solution of 1,6-dichloropermethylhexasilane (**3**) in hexane cooled to 0 °C, giving 1,8-diphenylpermethyloctasilane (**4**) in 83% yield. Treatment of a toluene solution of 1,8-diphenyloctasilane **4** cooled to 20 °C with trifluoromethanesulfonic acid followed by addition of a THF solution of phenylsilyllithium **2** to give 1,10-diphenylpermethyldecasilane (**5a**) in 88% yield. 1,10-Diphenyldecasilane **5a** was treated with trifluoromethanesulfonic acid in toluene at 20 °C to give 1,10-bis(trifluoromethanesulfonyl)permethyldecasilane (**5b**). To the resulting toluene solution, a solution of ethylmagnesium bromide in Et_2O was added dropwise at room temperature and the resulting mixture was allowed to react at 70 °C overnight to give 1,10-diethyldecasilane **1b** in 79% yield. 1,10-Dipropyldecasilane **1c** and 1,10-dibutyldecasilane **1d** were prepared by treatment of a solution of decasilane **5b** in toluene with a solution of the corresponding alkyllithiums in hexane at room temperature overnight in 64 and 70% yields, respectively. 1,10-Dialkyldecasilanes **1b-d** are a white waxy solid, and these compounds were successfully purified with a preparative HPLC. The spectral data for decasilane **1d** were described 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.



SCHEME 1

Mesomorphism

The thermal properties of decasilanes **1b-d** were examined by the combination of DSC measurements and polarized optical microscopy. The values for the transition temperatures and the associated enthalpies (ΔH) for these compounds are summarized in Table 1. For all the compounds, like decasilanes **1a**[3c], two endothermic peaks are observed on heating and two large exothermic peaks appear on cooling. At these temperature ranges between the transition peaks both on heating and on cooling, decasilanes **1b-d** show a texture similar to a lancet texture typical of a smectic B phase[3c,4]. The observation of the texture indicates that these decasilanes show the enantiotropic mesophase. Diethyldecasilane **1b** has the mesomorphic state in the range of 50-105 °C on heating and 106-49 °C on cooling. Dipropyldecasilane **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. Dibutyldecasilane **1d**, like **1c**, forms the mesophase in the range of 23-69 °C on heating and both the mesophase and the X phase in the range of 69-18 and 18-13 °C on cooling, respectively. Although the isotropization temperatures of decasilanes **1a-d** (114, 105, 87, and 69 °C, respectively) decrease monotonously with increasing length of the alkyl chains at the both ends of the decasilane unit, the mesomorphic

TABLE 1 Transition temperatures and enthalpies for 1,10-dialkylpermethyldecasilanes **1b-d**, $R[Si(CH_3)_2]_{10}R$

compd	R	transition temperatures / °C [ΔH / kJmol^{-1}] [a]
1b	C_2H_5	$\begin{tikzcd} K \arrow[rr, shift left, "50\ [11.9]"] & & M \arrow[ll, shift left, "49\ [11.7]"] \arrow[r, shift left, "105\ [14.1]"] & I \arrow[l, shift left, "106\ [14.0]"] \end{tikzcd}$
1c	C_3H_7	$\begin{tikzcd} K \arrow[rr, "22\ [22.1]"] & & M \arrow[r, shift left, "87\ [14.2]"] & I \arrow[l, shift left, "86\ [13.7]"] \\ & X \arrow[ul, "12\ [3.4]"'] \arrow[ur, "21\ [17.4]"'] & & \end{tikzcd}$
1d	C_4H_9	$\begin{tikzcd} K \arrow[rr, "23\ [28.6]"] & & M \arrow[r, shift left, "69\ [12.5]"] & I \arrow[l, shift left, "69\ [12.4]"] \\ & X \arrow[ul, "13\ [7.1]"'] \arrow[ur, "18\ [20.6]"'] & & \end{tikzcd}$

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

ranges for decasilanes **1b-d** (55, 65, and 46 °C, respectively) are wider than that for **1a** (32 °C). Interestingly, dipropyldecasilane **1c** and dibutyldecasilane **1d** form the mesophase at room temperature on cooling.

Molecular Alignment and Conformation

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**[3c], except for the layer spacings. An intense peak (100) and a weak peak (110) corresponding to $d_{100}/\sqrt{3}$ are observed in the wide angle region. These peaks are attributed to the reflections of the hexagonal lattice and the lattice constant a ($d_{100} \times 2/\sqrt{3}$) corresponds to the intermolecular distance between the nearest molecular chains. The intermolecular distances (the hexagonal lattice constant a = 7.85, 7.78, and 7.78 Å for **1b**, **1c**, and **1d**, respectively) are very close to that for **1a** (7.91 Å). In the small angle region, the X-ray patterns for **1b**, **1c**, and **1d**, unlike **1a**, show only peaks corresponding to the second and forth order reflections of the interdigitated layer. 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** 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}

TABLE 2 The *d*-spacings / Å and the lattice constant *a* / Å for 1,10-dialkylpermethyldecasilanes **1b-d**, $R[Si(CH_3)_2]_{10}R$, in the mesophase

compd	R	d_{002}	Δd_{002}	d_{004}	d_{100}	d_{110}	a
1b	C_2H_5	21.9	1.3	11.0	6.80	3.96	7.85
1c	C_3H_7	23.2	1.2	11.6	6.74	3.93	7.78
1d	C_4H_9	24.4		12.2	6.74	3.92	7.78

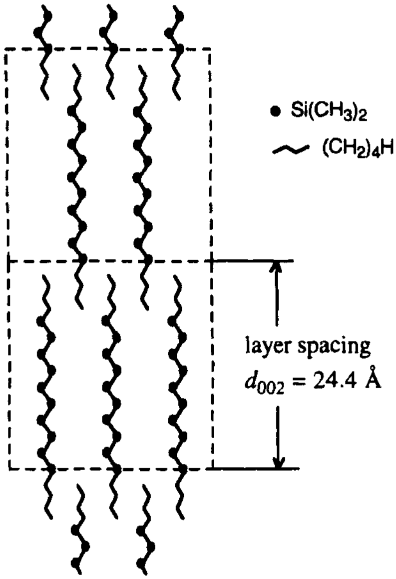


FIGURE 1 Schematic illustration of the multilayer interdigitated structure for decasilane **1d** in the mesophase.

= 1.53; d_{CC} = 1.24 Å, estimated from a molecular model. These results indicate that the oligosilane molecules of decasilanes **1b**-**d**, unlike **1a**, form a multilayer interdigitated structure, as illustrated in Figure 1. The molecular alignment for decasilanes **1b-d** are very similar to that for **1a**, except for the layer structure; the oligosilane molecules are hexagonally ordered and perpendicular to the layers. The alkyl and silicon chains of decasilanes **1b**-**d**, like **1a**, adopt almost all-*trans* conformations.

Electronic Absorption

Electronic absorption spectra of decasilanes **1a**-**d** were measured in the mesophase, in the liquid state, and in solution. 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. The spectral deta were listed in Table 3. The UV absorption of the decasilanes in the mesophase are of particular interest. Absorption bands with maxima at 292 (ε = 1700), 293 (ε

TABLE 3 Electronic spectral data (λ_{max} / nm [ε / $Lmol^{-1}cm^{-1}$]) for decasilanes **1a-d**, $R[Si(CH_3)_2]_{10}R$

compd	R	mesophase	liquid	solution
1a	CH_3	292 [1700]	279 [26000]	280 [40900]
1b	C_2H_5	293 [2000]	280 [26000]	281 [41400]
1c	C_3H_7	294 [1900]	280 [28000]	281 [41000]
1d	C_4H_9	294 [2200]	280 [25000]	281 [41100]

= 2000), 294 (ε = 1900), and 294 nm (ε = 2200) are observed for **1a-d** in the mesophase, respectively. 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). 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)[1d]. 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**. The interdigitated interactions between the alkyl chains in **1b** are weaker than those in **1c** and **1d**, because the alkyl chains in **1b** are shorter than those in **1c** and **1d**. Interestingly, the wave length of maximum absorption of **1a-d** in the mesophase is almost the same as that of **1a** in a 3-methylpentane glass at 77 K (λ_{max} = 294 nm)[1e].

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