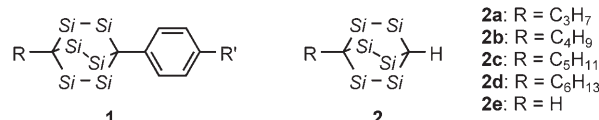


1-Alkyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octanes: Unconventional Class of Mesomorphic Columnar Compounds**

Masaki Shimizu,* Masanori Nata, Kenji Mochida, Tamejiro Hiyama, Seiji Ujiie,* Masafumi Yoshio, and Takashi Kato*

Liquid crystals have attracted much attention in the fields of material and bio-related science.^[1] The investigation of liquid-crystalline compounds with unconventional structures has gained growing interest aimed at the discovery of new ordered structures and/or new modes of self-assembly/self-organization, as well as the creation of new soft materials.^[2] Indeed, attention has been focused on columnar liquid-crystalline compounds, which generally consist of a conventional disc-shaped central core, such as benzene, triphenylene, truxene, or phthalocyanine, with long alkyl groups as flexible peripheral moieties attached to the core.^[3] Representative examples of unconventional columnar liquid-crystalline compounds that do not conform to such a structural prototype are polyhydroxy amphiphiles, including carbohydrates with long alkyl chains, pyramidal macrocycles, acyclic oligoamides, polycatenar compounds, laterally substituted rodlike molecules, and halogen-substituted indenenes.^[4] However, to our knowledge, no example of columnar liquid-crystalline com-

pounds is available which contains neither long alkyl groups nor aromatic rings, except for diisobutylsilanediol, where the columnar mesophase is formed through hydrogen-bonding interactions.^[5] Recently, we found that 1-alkyl-4-aryl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octanes **1** exhibited a columnar liquid-crystalline mesophase,^[6] which is in sharp contrast to 1-alkyl-4-aryl-bicyclo[2.2.2]octanes which exhibit nematic and/or smectic phases.^[7] We thus turned our attention to utilizing of the polysilacage framework itself as a mesogenic core (Scheme 1).^[8] Described herein are the properties of **2a–d**, which are a novel class of mesomorphic columnar compounds that lack both long alkyl chains and aromatic rings.



Scheme 1. 2,3,5,6,7,8-Hexasilabicyclo[2.2.2]octanes **1** and **2** (Si = SiMe₂).

Polysilacage compounds **2a–d** were prepared in good yields by deprotonation of 2,2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane (**2e**) with a superbase consisting of BuLi and *t*BuOK followed by alkylation with the appropriate alkyl iodide.^[9]

The mesomorphic properties of **2a–d** are summarized in Table 1 and Figure 1. On cooling from the isotropic phases, all compounds showed hexagonal dendritic textures without birefringence (Figure 1),^[10] which were characteristic of hexagonal columnar mesophases. Differential scanning calo-

Table 1: Thermal properties of **2a–d**.

2	Scan ^[a]	Mesomorphic properties (T [ΔH]) ^[b]
2a	heating	Cr 136 [2.8] Col _h 323 [1.6] I
	cooling	Cr 118 [−2.8] Col _h 323 [−1.4] I
2b	heating	G 165 Col _h 224 [0.2] I
	cooling	G 136 Col _h 222 [−0.2] I
2c	heating	G 64 Col _h 249 [3.5] I
	cooling	G 46 Col _h 231 [−3.5] I
2d	heating	Cr 194 [4.1] I
	cooling	Cr 120 [−1.8] Col _h 181 [−2.3] I

[a] For **2a–c**, Heating and cooling scans at 10 K min^{−1}. For **2d**, heating and cooling scans at 15 K min^{−1}. [b] Cr: crystal, Col_h: hexagonal columnar phase, I: isotropic phase, G: glass. T: temperature in °C, ΔH: transition enthalpy in kJ mol^{−1}.

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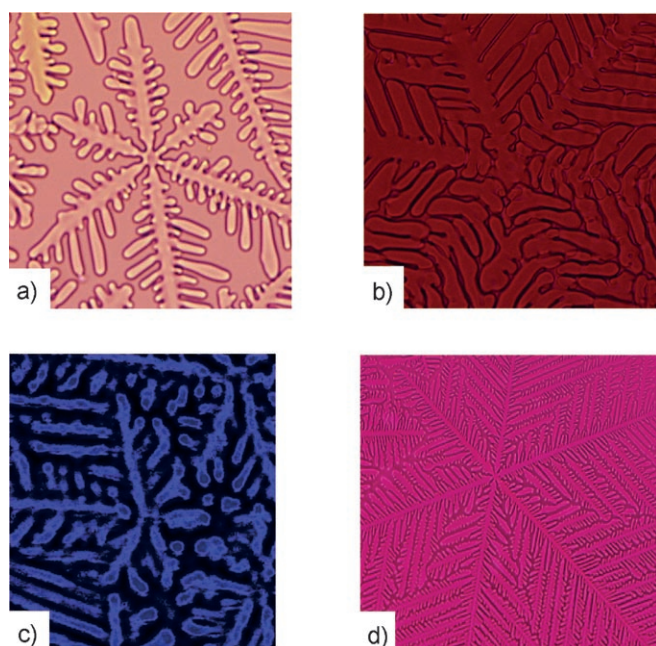


Figure 1. Polarizing optical photomicrographs of: a) **2a** at 280°C, b) **2b** at 210°C, c) **2c** at 170°C, and d) **2d** at 170°C.

rimetry (DSC) analysis revealed that the mesophases of **2a–c** were enantiotropic, while that of **2d** was monotropic. The DSC trace of **2a** is shown as an example in Figure 2. The enthalpies of the columnar–isotropic phase transition ranged from 0.2 to 3.5 kJ mol^{−1}, while the clearing points were relatively high. A glass transition was observed in the case of **2b** and **2c**.

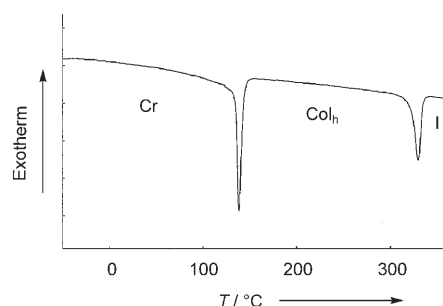


Figure 2. DSC trace of **2a** on heating (scan rate: 10°C min^{−1}).

The X-ray diffraction (XRD) data of **2a–d** are summarized in Table 2. The XRD pattern of **2c**, measured at 200°C (Figure 3a), showed reflections with *d*-spacings of 7.33, 4.41, 3.65, and 2.81 Å. The reciprocal spacing ratio of the four peaks are 1:√3:2:√7, from which the peaks can be assigned to the (100), (110), (200), and (210) reflections. This diffraction pattern is characteristic of a hexagonal columnar structure, and is consistent with the phase assignment from the dendritic texture shown in Figure 1. The presence of a sharp (001) reflection suggests an ordered arrangement in the columnar direction. A broad halo at 8.0–9.4 Å was observed which indicates diffuse scattering of the pentyl group. Meanwhile,

Table 2: X-ray diffraction data for the mesophase of **2a–2d**.

2	<i>T</i> [°C]	Lattice constants [Å]	<i>d</i> _{obs} [Å]	<i>d</i> _{calcd} [Å]	<i>hkl</i>
2a	250	<i>a</i> = 9.07	8.26	8.25	001
		<i>c</i> = 8.25	7.86		100
			4.12	4.12	002
			2.75	2.75	003
2b	155	<i>a</i> = 9.39	8.19		001
		<i>c</i> = 8.19	8.13		100
2c	200	<i>a</i> = 8.57	8.48		001
		<i>c</i> = 8.48	7.33	7.43	100
			4.41	4.29	110
			3.65	3.71	200
			2.81	2.81	210
			8.21		001
	25	<i>a</i> = 8.26	7.16		100
		<i>c</i> = 8.21	5.06		101
			4.32		110
			3.58		200
			2.76		210
			2.39		300
2d	150	<i>a</i> = 8.52	8.55		001
		<i>c</i> = 8.55	7.38		100
					100

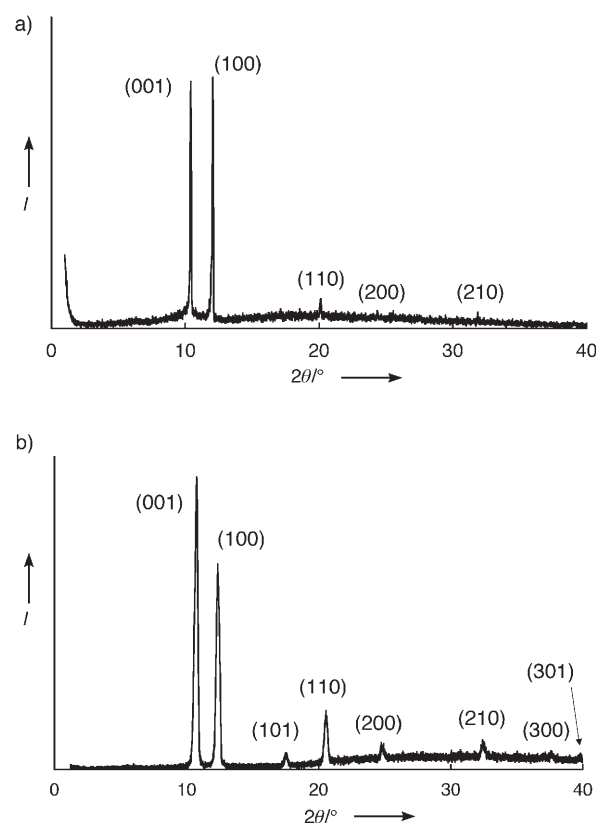


Figure 3. Wide-angle X-ray diffractogram of **2c** measured: a) at 200°C and b) at 25°C.

(101) and (301) reflections characteristic of three-dimensional ordered structures were observed in addition to the four peaks, when the XRD spectrum of **2c** was recorded at 25°C (Figure 3b). These results clearly indicate that the mesophase of **2c** is a columnar hexagonal phase, and not a plastic crystal.

The single-crystal structure of **2a** was consistent with a monoclinic space group with cell constants $a = 15.5080(13)$, $b = 9.4313(8)$, $c = 17.7357(14)$ Å, and $\beta = 93.5950(10)^\circ$.^[11] The packing diagram viewed along the b axis is shown in Figure 4.

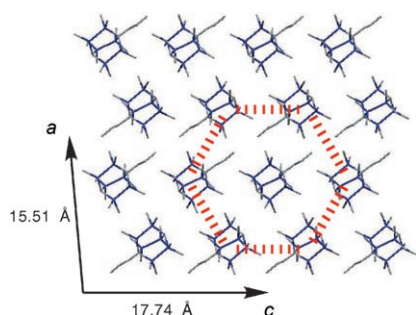


Figure 4. Packing diagram of a single crystal of **2a**.

Each molecule forms layers in which propyl groups in one layer are oriented in the same directions and the direction of the propyl groups are reversed in each successive layer. In particular, the arrangement of the polysililacage moieties appears to generate a hexagonal structure. Since the molecular shape of the polysililacage moiety (Figure 5a) looks

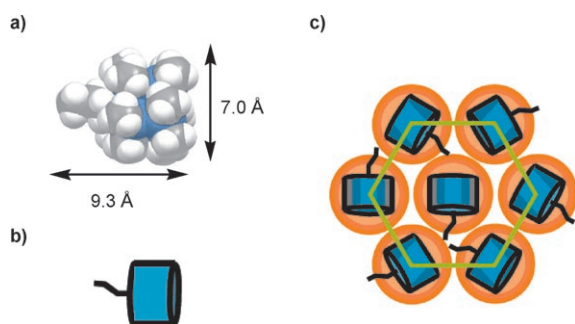


Figure 5. Space-filling model, graphical illustration, and plausible model for the molecular arrangement of **2a** in the mesophase.

almost like sphere, such a packing mode is probably the most favored to minimize the free volume in the crystal. From the molecular shape and the packing arrangement of the polysililacage compound in the single crystal, together with the XRD results of the mesophase, a plausible model for the molecular arrangement of **2a** in the mesophase is shown in Figure 5c. The transition from the crystal to the mesophase could be associated with the onset of molecular rotation around the b axis (the columnar axis) and the existence of the short alkyl chains might control the direction of rotation in the column.

In summary, we have described a new class of unconventional mesomorphic columnar compounds that contain neither long alkyl chains nor aromatic rings. Further studies on

the modification of the substituents on the silicon atoms of the polysililacage compounds as well as their application in functional materials are in progress.

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- [10] The samples are viscoelastic rather than simply viscous fluids.
- [11] **2a**: $\text{C}_{17}\text{H}_{44}\text{Si}_6$, crystal size $0.5 \times 0.5 \times 0.5 \text{ mm}^3$, space group $P2(1)/c$ (monoclinic), $a = 15.5080(13)$, $b = 9.4313(8)$, $c = 17.7357(14) \text{ \AA}$, $\beta = 93.5950(10)^\circ$, $V = 2588.9(4) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.070 \text{ g cm}^{-3}$, $\mu(\text{Mo}_{\text{K}\alpha}) = 0.322 \text{ mm}^{-1}$. Data were measured on a Bruker SMART APEX diffractometer ($\text{Mo}_{\text{K}\alpha}$ radiation, $\lambda = 0.71073 \text{ \AA}$) at 298 K, and the structure was solved by direct methods. Of 13663 reflections collected, 4796 were unique ($R_{\text{int}} = 0.0210$); data/restraints/parameters 4790/0/221; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0422$, $wR_2 = 0.1200$; R indices (all data): $R_1 = 0.0532$, $wR_2 = 0.1266$. CCDC-620199 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.