

Novel Liquid Crystalline Compounds Based on 4-Aryl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octanes

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We prepared novel cage compounds containing 1-alkyl-4-aryl-2,2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane and found that 1-alkyl-4-phenyl-substituted derivatives $n\text{-C}_n\text{H}_{2n+1}\text{C}(\text{SiMe}_2\text{SiMe}_2)_3\text{CPh}$ exhibited hexagonal columnar phase, characteristic of discotic liquid crystalline compounds, irrespective of the rod-like structure, when a substituent at the bridgehead position ranged from hydrogen to a pentyl group ($n = 0$ to 5).

Key words: bicyclo[2.2.2]octane, discotic, liquid crystal, mesogen, silicon

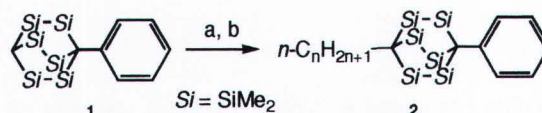
1. Introduction

We have recently established a facile route to 2,2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane.¹ Introduction of a functional group at bridgehead positions can be effected by metalation at the position with a superbases consisting of BuLi and *t*-BuOK followed by a reaction with an electrophile. Furthermore, cyclohexenylation of the polysilacage compound followed by aromatization allows us to prepare 1-phenyl-substituted 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane **1**.² On the other hand, incorporation of bicyclo[2.2.2]octane moiety into an organic molecule induces molecular rigidity and enhances thermal stability of the resulting compounds. As a bicyclic framework is often utilized as a core of calamitic liquid crystalline compounds,³ we explored potential of the silicon cage compounds as an analog of bicyclo[2.2.2]octane liquid crystalline compounds, report herein the synthesis and properties of polysilacage compounds, 1-alkyl-4-aryl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octanes **2**.

2. Results and Discussion

Treatment of a THF solution of **1** with a superbases in excess at $-42\text{ }^\circ\text{C}$ followed by the addition of an alkyl halide at $-42\text{ }^\circ\text{C}$ to room temperature gave the corresponding 1-alkyl-4-aryl-substituted cage compound (**2**) in good yields as shown in Table 1.

Table 1. Preparation of **2**.



a) BuLi (4.2 eq)/*t*-BuOK (4.0 eq), THF, $-42\text{ }^\circ\text{C}$, 1~2 h
b) $n\text{-C}_n\text{H}_{2n+1}\text{-I}$ (10 eq), $-42\text{ }^\circ\text{C}$ to room temperature, 1 d.

n	2	Yield (%)	n	2	Yield (%)
1	2a	90	5	2e	92
2	2b	91	6	2f	80
3	2c	95	7	2g	>99
4	2d	86	8	2h	82

Thermal properties of **1** and **2** were investigated by differential scanning calorimetry (DSC) with heating and cooling rates of $15\text{ }^\circ\text{C}/\text{min}$. Phase transition temperatures ($^\circ\text{C}$) and enthalpies ($\text{kJ}\cdot\text{mol}^{-1}$) are summarized in Table 2. Compounds **1** and **2a-e** ($n = 0$ to 5) showed mesophase between solid state and isotropic liquid, while no mesophase was observed with **2f-h** that contained a longer alkyl chain than a pentyl group.

Polarized light microscopy showed that, when heated, **1** and **2a-e** underwent phase transformation from anisotropic to isotropic. When **2a** was cooled slowly from isotropic melts, large domains of dendritic homeotropic texture appeared, typical for columnar mesophases (Figure 1a). The texture was, upon further

Table 2. Phase transition temperature ($^{\circ}\text{C}$) and enthalpy ($\text{kJ}\cdot\text{mol}^{-1}$) of **1** and **2**

	heating			cooling		
	Cr	Col _h	I	Cr	Col _h	I
1	• 216.6 (6.09)	• 255.9 (1.80)	•	• 130.8 (-8.53)	• 244.1 (-2.05)	•
2a	• 96.1 (5.01)	• 307.0 (2.24)	•	• 80.4 (-4.34)	• 296.5 (-3.25)	•
2b	• 96.6 (1.70)	• 293.4 (3.55)	•	• 75.9 (-1.54)	• 282.3 (-3.64)	•
2c	• 158.4 (4.88)	• 291.3 (9.08)	•	• 93.9 (-6.59)	• 264.6 (-10.66)	•
2d	• 277.4 (2.06)	• 306.6 (13.34)	•	• 246.6 (-14.29)		•
2e	• 207.8 (1.51)	• 234.7 (5.55)	•	• 170.7 (-9.13)		•
2f	• 213.3 (6.75)		•	• 142.4 (-11.42)		•
2g	• 206.6 (13.14)		•	• 152.6 (-15.90)		•
2h	• 163.8 (12.59)		•	• 89.4 (-14.68)		•

cooling, developed to typical hexagonal columnar ice crystal texture (Figure 1b).

On cooling from the melt of **2e**, tree texture was observed at 200 $^{\circ}\text{C}$, which was characteristic to hexagonal columnar mesophase (Figure 2).

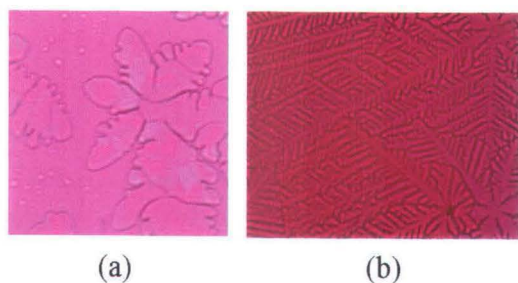


Figure 1. Polarized light microscopic images of **2a** (a) at 290 $^{\circ}\text{C}$, (b) at 280 $^{\circ}\text{C}$.

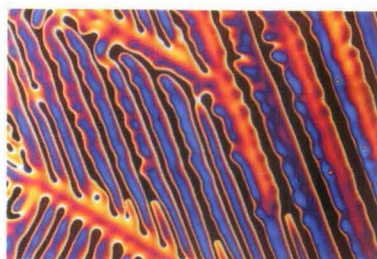


Figure 2. Photomicrograph of **2e** at 200 $^{\circ}\text{C}$.

In summary, 1-alkyl-4-phenyl-substituted derivatives were found to exhibit hexagonal columnar phase, characteristic of discotic liquid crystalline compounds, with an alkyl group ranging from a methyl to a pentyl group. Noteworthy is that the polysiloxane compounds exhibit discotic liquid crystallinity irrespective of the rod-like structure.

Further studies on development of novel liquid crystalline compounds utilizing 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane as a core are in progress.

3. References

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