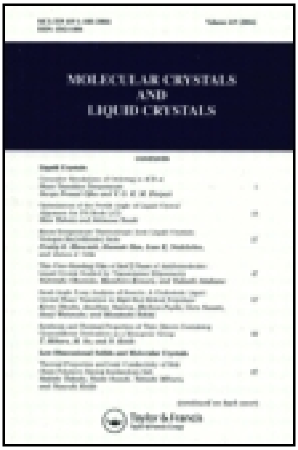

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

2,3,5,6,7,8-Hexasilabicyclo[2.2.2]octane-derived Columnar Liquid Crystals

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To cite this article: Masaki Shimizu, Masanori Nata, Kotaro Watanabe, Tamejiro Hiyama & Seiji Ujiie (2005): 2,3,5,6,7,8-Hexasilabicyclo[2.2.2]octane-derived Columnar Liquid Crystals, Molecular Crystals and Liquid Crystals, 441:1, 237-241

To link to this article: http://dx.doi.org/10.1080/154214091009833

Mol. Cryst. Liq. Cryst., Vol. 441, pp. 237–241, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214091009833

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The title polysilacage compounds with p-alkylphenyl or p-cyanophenyl-substituent were prepared starting with 1-phenyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane; p-pentylphenyl- and p-(2-methylpentyl)phenyl-substituted polysilacages exhibited columnar lamellar phase particularly, whereas cyanophenyl-substituted derivatives showed hexagonal columnar mesophases in spite of the rod-like structures. Introduction of a cyano group resulted in the enhancement of the structural order of the mesophase as compared with the parent cage compounds.

Keywords: bicyclo[2.2.2]octane; columnar liquid crystal; cyano; silicon

A series of phenyl-substituted bicyclo[2.2.2]octanes constitute a class of nematogens. For example, 1-alkyl-4-(4-cyanophenyl)bicyclo[2.2.2]-octanes reportedly exhibit nematic phases at higher and wider temperature ranges than the analogs having a benzene or cyclohexane mesogen in lieu of the cage-like core [1].

The title compound 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**), a silicon analog of the cage-like core, was prepared some years ago to give a single crystal in which the molecule formed a tilted layered structure like smectic C phase (Fig. 1) [2]. Metalation at the bridgehead of **1** with BuLi/*t*-BuOK

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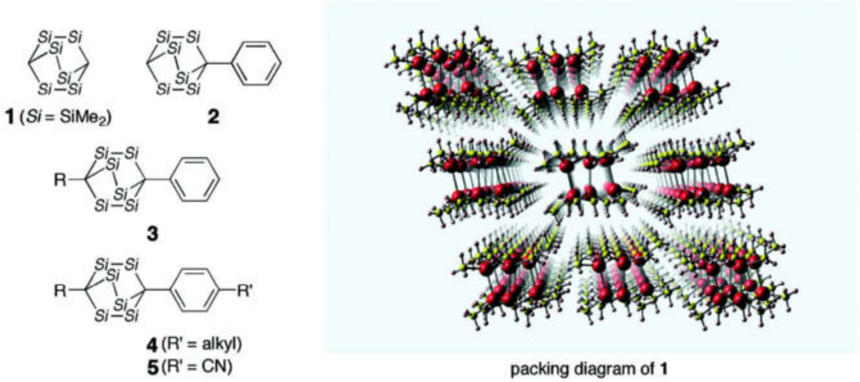
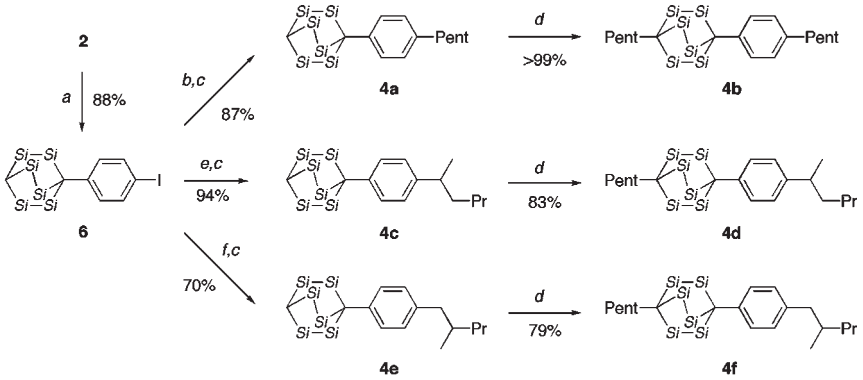


FIGURE 1 Packing diagram of **1**.

followed by alkylation with 3-bromocyclohexene and dehydrogenative aromatization allowed us to obtain the phenyl-substituted polysilacage compound **2** [3]. Additionally, the alkyl-substituted derivatives **3**, prepared by the similar alkylation, exhibited hexagonal columnar ($\mathrm{Col_h}$) and rectangular columnar ($\mathrm{Col_r}$) phases in spite of the rod-like structure [4]. To gain further insight into the character of 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane-derived liquid crystals, we planned to introduce an alkyl or cyano group at the *para*-position of the phenyl ring in **2**. Reported herein are the preparation and liquid crystalline properties of *p*-alkylphenyl- and *p*-cyanophenyl-substituted polysilacage compounds **4** and **5**, respectively.

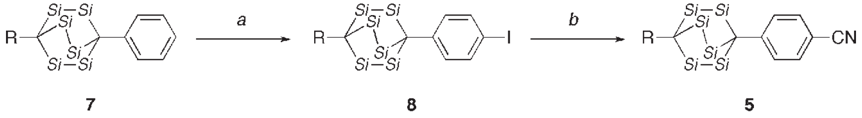
Polysilacage compounds **4** were prepared according to the synthetic route shown in Scheme 1. Treatment of **2** with molecular iodine in the presence of silver trifluoroacetate selectively gave iodide **6** in 88% yield. Hagihara-Sonogashira coupling of **6** with 1-pentyne afforded **4a**, which was transformed to **4b** quantitatively by superbase treatment followed by alkylation with pentyl iodide. Branched hexyl groups were introduced to **6** in good yields by Suzuki-Miyaura coupling reaction with the corresponding 1-alkenyl(pinacolato)boranes, followed by hydrogenation and pentylation as described above, to afford **4c–4f**.

The preparation of cyanide **5** is illustrated in Scheme 2. Since a cyano group does not tolerate the metalation conditions for the bridgehead alkylation, introduction of a cyano group was realized at the last step. Thus, iodination of **2** and of the alkylated cage compounds **7b** and **7c** followed by cyanation with copper cyanide at the refluxing temperature of DMF gave **5a–5c** in good yields.



SCHEME 1 Preparation of polysilacage compounds **4** (Pr: n-C_3H_7; Pent: n-C_5H_{11}; B_{pin}: (pinacolato)boryl). Reagents and conditions: a) I_2 (1.2 eq), AgO_2CCF_3 (3.0 eq), $CHCl_3$, rt. b) $(PPh_3)_2PdCl_2$ (10 mol%), CuI (10 mol%), Et_2NH, rt. c) H_2 (1 atm), Pd/C, AcOEt, rt. d) BuLi (4.2 eq)/t-BuOK (4 eq), THF, −42°C, then Pent–I (10 eq), −42°C to rt. e) $Me(B_{pin})C{=}CHPr$ (1.5 eq), $Pd(PPh_3)_4$ (10 mol%), KOH (1.5 eq), dioxane, 90°C. f) $H(B_{pin})C{=}C(Me)Pr$ (1.5 eq), $Pd(PPh_3)_4$ (10 mol%), KOH (1.5 eq), dioxane, 70°C.

Differential scanning calorimetry (DSC) data of **4** and **5** are summarized in Table 1. p-Alkylphenyl derivatives **4a** and **4e** as well as cyanides **5a–5c** showed mesophases, while no mesophase was observed for **4b–4d** and **4f**. The polarized optical micrographs of the mesophases for **4a**, **4e**, and **5a–c** are shown in Figure 2. A platelet texture for **4a** and a broken-fan-shaped texture for **4e** were observed, both of which are typical for columnar lamellar phase. Meanwhile, the dendritic textures having a homeotropic alignment appear for all of **5** on cooling from the isotropic melt, indicating hexagonal columnar



7	R	8	Yield (%)	5	Yield (%)
2	H	**6**	88	**5a**	85
7b	Me	**8b**	>99	**5b**	90
7c	Et	**8c**	60	**5c**	96

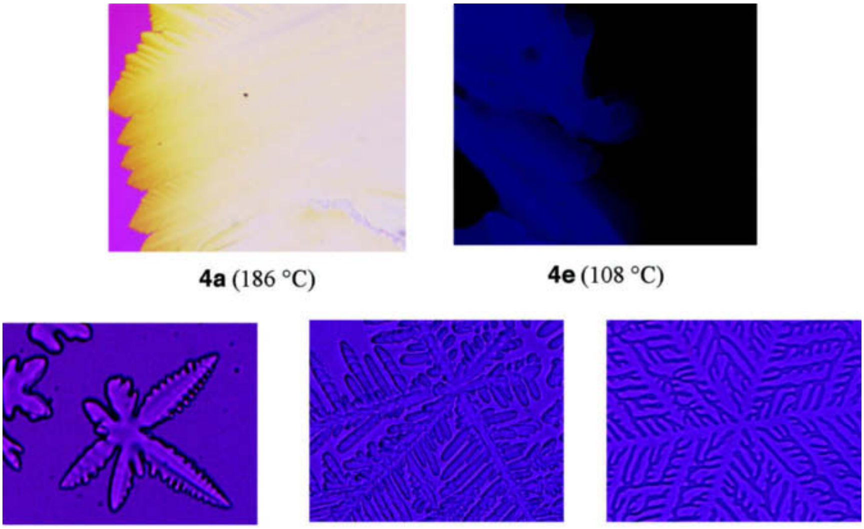
SCHEME 2 Preparation of cyanide **5**. Reagents and conditions: a) I_2 (1.2 eq), AgO_2CCF_3 (3.0 eq), $CHCl_3$, rt. b) CuCN (1.5 eq), DMF, reflux.

TABLE 1 Phase Transition Temperature (°C) and Enthalpy ($kJ \cdot mol^{-1}$) of **4** and **5**[a]

	Heating	Cooling
4a	Cr_1 82.0 (0.55) Cr_2 120.0 (1.95) Col_L 189.4 (13.91) I	Cr_1 70.9 (–0.74) Cr_2 104.7 (–18.13) I
4b	Cr_1 20.4 (1.50) Cr_2 177.9 (13.81) I	Cr_1 9.2 (–1.58) Cr_2 115.4 (–13.28) I
4c	Cr 121.9 (21.51) I	Cr 93.5 (–21.76) I
4d	Cr 147.4 (11.14) I	Cr 30.4 (–10.18) I[b]
4e	Cr 97.2 (6.35) Col_L 109.1 (1.85) I	Cr_1 39.5 (–2.65) Cr_2 62.5 (–11.00) I
4f	Cr 100.7 (12.10) I	Not determined
5a	Cr 156.5 (4.26) Col_h 328.7 (10.10) I	Cr 59.3 (–1.50) Col_h 307.7 (–10.30) I
5b	Cr 209.9 (3.99) Col_h 329.1 (4.78) I	Cr 167.3 Col_h 307.2 (–4.76) I
5c	Cr 153.6 (4.58) Col_h 328.8 (7.17) I	Cr 87.2 (–3.54) Col_h 319.4 (–7.02) I

[a] Scan rate: 15°C/min.

[b] Scan rate: 5°C/min.



4a (186 °C) **4e** (108 °C)

5a (220 °C) **5b** (327 °C) **5c** (305 °C)

FIGURE 2 Polarized light microscopic images of **4a**, **4e**, and **5**.

mesophase. The introduction of a cyano group at *para*-position of the phenyl group was found to remarkably enhance the stability of the columnar phases by comparison with the mesogenic behavior of **3** [4]. In addition, **5** sharply contrasts to 1-alkyl-4-(4-cyanophenyl)bicyclo-[2.2.2]octanes that exhibit a nematic phase [1]. These results clearly disclose that the phenyl-substituted polysilacage mesogen has a high tendency to form columnar structure in spite of the rod-like shape.

In summary, we have demonstrated that the polysilacage compounds with *p*-alkylphenyl exhibit a columnar lamellar phase, while the *p*-cyano-derivatives **5** prefer the formation of hexagonal columnar phase. Further studies on 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane-derived liquid crystal compounds are in progress.

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