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Journal of Organometallic Chemistry 685 (2003) 138–144
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

2,3,5,6,7,8-Hexasilabicyclo[2.2.2]octane-1-carboxylic acids and esters: preparation and structure

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Received 27 December 2002; received in revised form 7 March 2003; accepted 10 March 2003

Abstract

Polysilacage acid $HC(SiMe_2SiMe_2)_3CCO_2H$ was prepared quantitatively by deprotonation of $HC(SiMe_2SiMe_2)_3CH$ by a superbase in excess followed by trapping with CO_2. The acid allowed to disclose X-ray analysis of hydrogen-bonded dimers that preferred pairs of the same enantiomeric isomers. Cage diacid $HO_2CC(SiMe_2SiMe_2)_3CCO_2H$ also was prepared. Esterification of the acids was found to proceed in good yields via the Mitsunobu conditions using diisopropyl azodicarboxylate.

Keywords: Bicyclo[2.2.2]octane; Cage compound; Cage acid; Cage ester; Mitsunobu reaction; Silicon

1. Introduction

In general, a bicyclo[2.2.2]octane moiety incorporated in an organic molecule induces molecular rigidity and enhances thermal stability. Therefore, such a bicyclic ring is often utilized as a mesogen of calamitic liquid crystalline compounds as well as molecular rods [1].

We have recently established an efficient route to 2,2,3,3,5,5,6,6,7,7,8,8-docecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane (**1**, Fig. 1) [2]. Functionalization of the polysilacage compound can be effected by metalation at the bridgehead position with a superbase consisting of BuLi and *t*-BuOK and subsequent reaction with such an electrophile as chlorosilane, chlorostannane, alkyl halide, bromine, iodine, or diphenyldisulfide [2a]. In particular, cyclohexenylation at the brigehead position followed by dehydrogenation allows us to prepare phenyl-substituted polysilacage molecules [3]. Among functionalized cage compounds, 1-pentyl-4-phenyl derivative **2** was found to exhibit tree texture characteristic to discotic hexagonal phase, inspite of the rod-like shape of **2**. This observation clearly indicates that substitution of carbons with silicons in cage framework can induce novel and unique properties of the resulting compounds.

In order to extend the possibility of novel liquid crystalline compounds based on 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane, we turned our attention to polysilacage (di)acids and (di)esters **3**–**6**, because carboxylic acids can be liquid crystals by forming hydrogen-bonded dimers and ester functionality is often utilized as a linking group in liquid crystals. Hence, development of preparative routes to polysilacage acids and esters and structural examination of the cage acids are crucial for further exploration of novel materials based on the cage acid derivatives. Here, we report the preparation and structure of the cage acids and esterification.

2. Results and discussion

2.1. Preparation and structure of polysilacage acid 3

Treatment of **1** (1 mol) with BuLi (4 mol) and *t*-BuOK (4 mol) in THF at −42 °C followed by bubbling of CO_2 gas gave 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane-1-carboxylic acid **3** as a colorless solid (dec. 165 °C) in 99% yield (Eq. 1). Diacid **4** was not produced at all despite the presence of a superbase in excess [2a].

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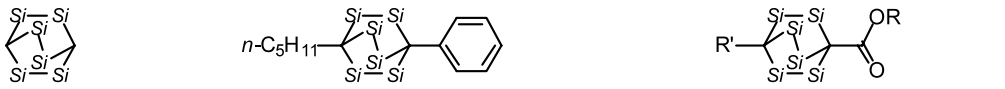
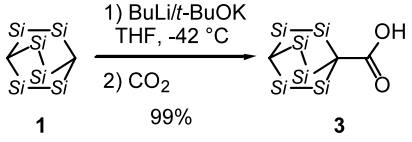
0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00161-X



1 **2**

3 (R = R' = H)
4 (R = H, R' = CO_2H)
5 (R = alkyl, 2-alkenyl, 2-alkynyl, R' = H)
6 (R = 2-alkenyl, R' = CO_2R)

Fig. 1. *Si* = $SiMe_2$.



1 **3** (1)

Si = $SiMe_2$

The carbonyl stretching absorption of **3** in infrared (IR) spectroscopy appeared at 1640 cm^{-1}. Since the absorptions of most alkanoic acids range from 1700 to 1730 cm^{-1} and conjugation is known to move the absorption to a lower frequency [4], σ–π conjugation between the cage moiety and the carbonyl group in **3** is clearly demonstrated.

Cage acid **3** crystallized from hexane in the monoclinic space group *C*2/*c* [5]. In the solid state, the molecule was axially chiral because hexasilabicyclo[2.2.2]octane framework was distorted from an ideal conformation of bicyclo[2.2.2]octane in a right- or left-handed manner. The left-handed molecular structure of **3** is shown in Fig. 2. The carboxyl carbonyl and one of silicon-bridgehead carbon bonds formed to be eclipsed. Dihedral angles of Si–C(1)–C(4)–Si ranged from 16.9 to 19.6° which were larger than those of **1** (12°), indicating that introduction of a carboxyl group at a bridgehead position made the hexasilabicyclo[2.2.2]octane framework more distorted.

Packing diagram of **3** is shown in Fig. 3. Each chiral molecule was hydrogen-bonded with the same enantiomer to form dimers. In other words, a right-handed molecule dimerized with a right-handed one, while a left-handed one was self-assembled with a left-handed enantiomer. Two kinds of dimers, respectively, made

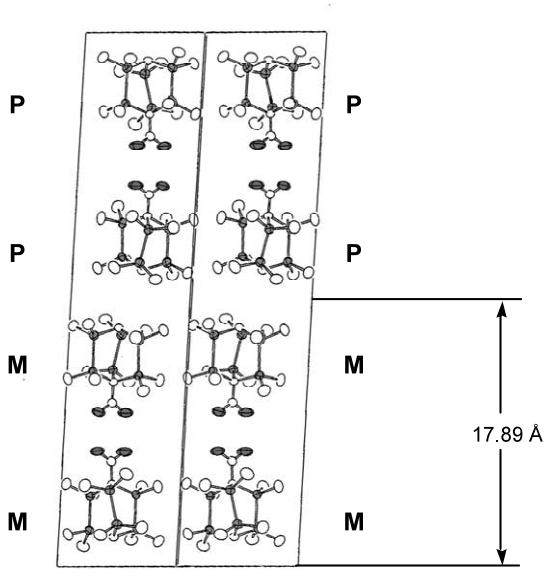
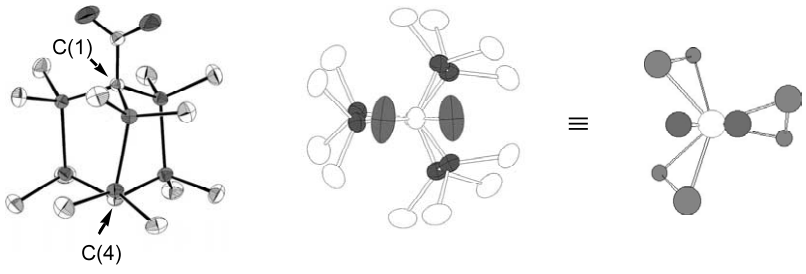


Fig. 3. Packing diagram of **3** (M = right-handed **3**, P = left-handed **3**).

layers that were 17.89 Å thick and alternatively stacked in a single crystal.

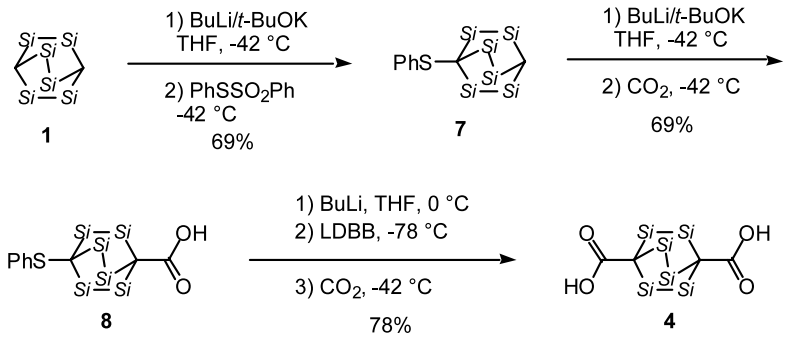
2.2. Preparation of polysilacage diacid **4**

Preparation of diacid **4** was also studied. Direct carboxylation of **3** initially attempted by treatment of **3** with the superbase and then CO_2 gas resulted in the decomposition of **3**. Therefore, we examined an indirect route to **4** (Scheme 1). Thus, **1** was firstly converted into phenylthio derivative **7** by treatment with the superbase and then with $PhSSO_2Ph$ [6] in 69% yield. The sequence of metalation and carboxylation gave acid **8** in 69%



side view *top view* left-handed molecule (**P**)

Fig. 2. Molecular structure of left-handed **3**.

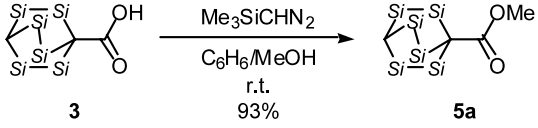


Scheme 1.

yield. Finally, a lithium salt of **8** generated by treatment with BuLi in THF was reduced with lithium 4,4′-di(*tert*-butyl)biphenylide [7] and carboxylated with CO_2 gas to produce **4** in 78% yield as a solid material. Although recrystallization of **4** was attempted in various ways, no single crystals suitable for X-ray analysis were obtained.

2.3. Esterification of polysilacage acids 3 and 4 under Mitsunobu conditions

With cage (di)acids **3** and **4** in hand, we next scrutinized their esterification. Cage acid **3** reacted with Me_3SiCHN_2 in benzene/methanol at room temperature to give methyl ester **5a** in 93% yield (Eq. 2), while condensation with methanol in the presence of oxalyl chloride or isobutyl chloroformate, or with phenol using dicyclohexylcarbodiimide as a dehydrating agent resulted in the decomposition of the polysilacage moiety to yield a complex mixture.



(2)

These results indicate that nucleophilic attack at the carbonyl carbon in **3** is quite difficult to proceed probably due to severe steric hindrance at the bridgehead position surrounded by three $SiMe_2$ groups. On the other hand, nucleophilic reaction of the carboxyl oxygen is possible. Treatment of **3** or **4** with cyclohex-2-ene-1-ol in the presence of triphenylphosphine and dimethyl azodicarboxylate [8] in THF gave ester **5b** or **6b** in 89 or 94% yield, respectively, after purification using gel permeation chromatography (GPC) (Table 1 and Eq. 3). However, esterification with such alcohols as (*E*)- or (*Z*)-pent-2-en-1-ol, dodec-2-yn-1-ol, octan-1-ol, and (*S*)-1-phenylethanol under the same conditions afforded the corresponding products less efficiently as shown in Table 1. Since consumption of acid **3** and decomposition of the polysilacage framework were observed by ^{1}H-NMR of the crude products, a betaine intermediate generated from triphenylphosphine and dimethyl azodicarboxylate might attack silicons and cleave the framework of **3**. Then, we envisaged that use of bulkier dialkyl azodicarboxylate would retard such undesirable process. Actually, yields of esters **5** increased simply by switching dimethyl azodicarboxylate to *diisopropyl* azodicarboxylate as demonstrated in Table 1. Thus, esters **5c**, **5d** and **5g** were isolated in slightly enhanced yields (59, 69 and 82%, respectively), while propargylic ester **5e** and alkyl ester **5f** were produced in considerably improved yields (92 and 78%).

Propargylic ester **5e** decomposed upon heating (decomposition point 76 °C) while alkyl and 2-alkenyl esters **5** were thermally stable (m.p.: **5a**, 180 °C; **5b**, 97 °C; **5c**, 106 °C; **5d**, 134 °C; **5f**, 73.5–74.6 °C; **5g**, 131 °C). No alkyl and 2-alkenyl esters, however, exhibited liquid crystallinity presumably because most of rod-like liquid crystals consisted of two or more rings. Hence, introduction of ring moieties into polysilacage esters is considered to be rational for further exploration of liquid crystals based on the cage acid derivatives.

3. Experimental

All temperatures were not corrected. Melting points were determined using a YANAKO MP-500D apparatus. All manipulations of oxygen- and moisture-sensitive materials were conducted with the standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). ^{1}H-NMR spectra were measured on a Varian Mercury 200 (^{1}H, 200 MHz) spectrometer. Chemical shifts of ^{1}H-NMR are expressed in parts per million downfield relative to an internal tetramethylsilane ($\delta = 0$ ppm) or chloroform ($\delta = 7.26$ ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet. ^{13}C-NMR spectra were measured on a Varian Mercury 200 (^{13}C, 50 MHz) and JEOL JMN ECP-500 (^{13}C, 125 MHz) spectrometer with tetramethylsilane as an internal standard ($\delta = 0$ ppm). ^{29}Si-NMR spectra were measured on a JEOL EX-270 (^{29}Si, 54 MHz) or JEOL JMN ECP-500 (^{29}Si, 99 MHz) spectrometer with tetramethylsilane as an internal standard ($\delta = 0$ ppm). IR spectra were

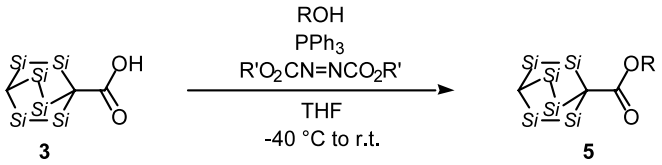
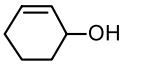
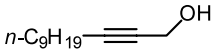
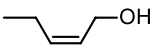
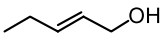
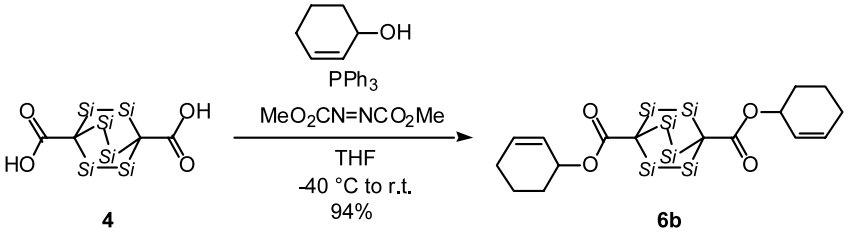


Table 1. Esterification[a] of cage acid **3**

ROH	R'	5	Yield[b] (%)	ROH	R'	5	Yield[b] (%)
	Me	**5b**	89		Me	**5e**	29
	i-Pr		80		*i*-Pr		92
	Me	**5c**	44	n-C_8H_{17}–OH	Me	**5f**	28
	i-Pr		59		*i*-Pr		78
	Me	**5d**	66		Me	**5g**	63
	i-Pr		69		*i*-Pr		82

[a] acid **3** (0.1 mmol), ROH (0.1 mmol), PPh_3 (0.1 mmmol), and $R'O_2CN{=}CNCO_2R'$ (0.1 mmol) were used.
[b] Isolated yield.



(3)

recorded on a Shimadzu FTIR-8400 spectrometer. GC–MS analyses were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. FAB-MS analyses were performed with a JEOL JMS-HX110A spectrometer using 3-nitrobenzyl alcohol or thiogrycerol as matrix. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} and R_f values were given. Column chromatography was carried out using Wakogel C-200. Preparative recycling GPC was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H columns (chloroform was used as an eluent). Cooling a reaction vessel at -78 and -40 °C was effected using methanol with dry ice. Ethereal solvents like THF, and diethyl ether were distilled from benzophenone and sodium under an argon atmosphere. Butyllithium was purchased from Sigma-Aldrich Co. Inc. and titrated before use with *N*-pivaloyl-*o*-toluidine as an indicator.

3.1. Synthesis 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-1-carboxylic acid (3)

To a suspension of **1** (75 mg, 0.20 mmol) and *t*-BuOK (94 mg, 0.84 mmol) in THF (3.0 ml) was added BuLi (1.54 M in hexane, 0.52 ml, 0.80 mmol) at −42 °C. The reaction mixture was stirred for 1 h at −42 °C and then CO_2 gas was bubbled for 1 h before quenching with 1 M HCl aqueous solution. The aqueous layer was extracted with ethyl acetate (twice) and chloroform (twice). The combined organic layer was neutralized with saturated aqueous $NaHCO_3$ solution, washed with saturated aqueous NaCl solution, and dried over anhydrous sodium sulfate. Removal of organic solvent by rotary evaporator under reduced pressure followed by column chromatography on silica gel (hexane and then hexane/ethyl acetate 10:1) afforded **3** (83 mg, 99%).

Colorless solid. M.p.: 165 °C (dec.). ^{1}H-NMR: δ 0.07 (s, 1H), 0.23 (s, 18H), 0.31 (s, 18H). ^{13}C-NMR: δ 1.7, 3.1, 3.3, 178.8. ^{29}Si-NMR: δ −19.5, −21.4. IR: ν_{max} 3450, 2920, 2824, 1640, 1370, 1250, 1220, 965, 810, 678, 660 cm^{-1}. FAB LRMS: *m/z* 421[M^++3], 420 [M^++2], 419 [M^++1], 418 [M^+], 401, 377, 261, 129, 73. FAB HRMS: Calc. for $C_{15}H_{39}O_2Si_6$ [M^++1]: 419.1566. Found: 419.1555.

3.2. Synthesis of 1-phenylthio-2,2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane (7)

To a suspension of **1** (0.75 g, 2.0 mmol) and *t*-BuOK (0.90 g, 8.0 mmol) in THF (20 ml) was added BuLi (1.49 M in hexane, 5.4 ml, 8.0 mmol) at −42 °C. The resulting mixture was stirred for 1 h at −42 °C, treated with a solution of $PhSSO_2Ph$ (3.0 g, 12 mmol) in THF (5.0 ml) at −42 °C, and allowed to warm to room temperature. Quenching with saturated aqueous NH_4Cl solution was followed by the extraction of aqueous layer with diethyl ether (twice). The combined organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) afforded **7** (0.67 g, 69% yield).

Colorless solid. M.p.: 208–210 °C. ^{1}H-NMR: δ −0.13 (s, 1H), 0.20 (s, 18H), 0.24 (s, 18H), 7.24–7.31 (m, 3H), 7.72–7.77 (m, 2H). ^{13}C-NMR: δ 1.1, 3.7, 20.2, 128.2, 128.7, 134.6, 138.6. ^{29}Si-NMR: δ −20.1, −71.6. IR: ν_{max} 2982, 2943, 2895, 2831, 1468, 1437, 1253, 970, 810, 752, 708, 679, 653, 590 cm^{-1}. FAB LRMS: *m/z* 486 [M^++4], 485 [M^++3], 484 [M^++2], 483[M^++1], 482 [M^+], 481[M^+−1], 467, 405, 373, 73. FAB HRMS: Calc. for $C_{20}H_{42}S_1Si_6$: 482.1623. Found: 482.1616.

3.3. Synthesis of 2,2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-4-phenylthio-2,3,5,6,7,8-hexasilabicyclo-[2.2.2]octane-1-carboxylic acid (8)

To a suspension of **7** (0.24 g, 0.50 mmol) and *t*-BuOK (0.22 g, 2.0 mmol) in THF (8.0 ml) was added BuLi (1.56 M in hexane, 1.3 ml, 2.0 mmol) at −42 °C. The reaction mixture was stirred for 1 h at −42 °C and CO_2 gas was bubbled for 1 h before quenching with 1 M HCl aqueous solution. The aqueous layer was extracted with ethyl acetate twice. The combined organic layer was washed with saturated aqueous NaCl solution and dried over anhydrous sodium sulfate. Removal of organic solvent by rotary evaporator under reduced pressure followed by column chromatography on silica gel (hexane/ethyl acetate 4:1) afforded **8** (0.21 g, 78% yield).

Colorless solid. M.p.: 175 °C. ^{1}H-NMR: δ 0.27 (s, 18H), 0.31 (s, 18H), 7.20–7.33 (m, 3H), 7.73–7.76 (m, 2H). ^{13}C-NMR: δ 1.1, 1.8, 18.9, 29.7, 128.4, 129.0, 133.9, 138.6, 180.0. ^{29}Si-NMR: δ −17.2, −17.3. IR: ν_{max} 2986, 2947, 2899, 2361, 1643, 1254, 1220, 978, 814, 685, 658 cm^{-1}. FAB LRMS: *m/z* 528 [M^++2], 527 [M^++1], 526 [M^+], 525, 509, 417, 401, 329, 261, 73, 59. FAB HRMS: Calc. for $C_{21}H_{43}O_2S_1Si_6$ [M^++1]: 527.1599. Found: 527.1602.

3.4. Synthesis 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-1,4-dicarboxylic acid (4)

To a solution of **8** (0.54 g, 1.0 mmol) in THF (20 ml) was added BuLi (1.49 M in hexane, 0.70 ml, 1.0 mmol) at 0 °C. The resulting solution was stirred for 10 min at 0 °C, cooled to −78 °C, and treated with lithium 4,4′-di-*tert*-butylbiphenylide (prepared from lithium dispersion (30 wt.%, 0.20 g, 29 mmol) and 4,4′-di-*tert*-butylbiphenyl (2.7 g, 10 mmol) in THF (20 ml)). The reaction mixture was stirred for 4 h at −78 °C before bubbling of CO_2 gas for 1 h at −78 °C. Quenching with 5 M HCl aqueous solution followed by usual workup gave a crude product, which was purified by column chromatography on silica gel ($CHCl_3$/MeOH 10:1) to produce **4** (0.36 g, 78% yield).

Colorless solid. M.p.: >300 °C. ^{1}H-NMR (THF-d_8): δ 0.33 (s, 36H). ^{13}C-NMR (THF-d_8): δ 2.1, 175.2. ^{29}Si-NMR (THF-d_8): δ −19.7. IR: ν_{max} 2910, 2850, 1640, 1458, 1365, 1250, 1205, 970, 875, 858, 803, 660 cm^{-1}. FAB LRMS: *m/z* 464 [M^++2], 463 [M^++1], 462 [M^+], 461 [M^+−1], 445, 73. FAB HRMS: Calc. for $C_{16}H_{37}O_4Si_6$ [M^+−1]: 461.1308. Found: 461.1314.

3.5. Synthesis of methyl 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-carboxylate (**5a**)

To a suspension of **3** (0.39 mg, 0.93 mmol) in benzene (8.0 ml) and MeOH (3.0 ml) was added trimethylsilyldiazomethane (2 M in hexanes, 2.3 ml, 4.6 mmol) at room temperature. The reaction mixture was stirred for 1 h at room temperature and quenched with acetic acid. The resulting mixture was concentrated in vacuo to afford a crude product. Purification by column chromatography on silica gel (hexane/ethyl acetate 5:1) gave rise to **5a** (0.40 g, 93% yield).

Colorless solid. M.p.: 180 °C. ^{1}H-NMR: δ −0.10 (s, 1H), 0.21 (s, 18H), 0.26 (s, 18H), 3.62 (s, 3H). ^{13}C-NMR: δ 1.7, 3.2, 3.3, 25.6, 50.9, 174.8. ^{29}Si-NMR: δ −21.4, −19.7. IR: ν_{max} 2984, 2945, 2897, 2831, 1682, 1425, 1396, 1256, 1167, 970, 926, 812, 712, 683, 664, 590 cm^{-1}. FAB LRMS: *m/z* 435 [M^{+}+3], 434 [M^{+}+2], 433 [M^{+}+1], 417, 373, 307, 129, 73. FAB HRMS: Calc. for $C_{16}H_{41}O_2Si_6$[M^{+}+1]: 433.1722. Found: 433.1725.

3.6. Typical procedure for esterification of cage acid **3** with diisopropyl azodicarboxylate

To a suspension of triphenylphosphine (26 mg, 0.10 mmol) in THF (1.0 ml) was added isopropyl azodicarboxylate (20 mg, 0.10 mmol) at −40 °C. The reaction mixture was stirred for 10 min at −40 °C, and an alcohol was added (0.10 mmol) at −40 °C. The resulting mixture was stirred for additional 10 min at −40 °C, treated with a solution of **3** (0.10 mmol) in THF (1.0 ml), allowed to warm to room temperature gradually, and filtered through a pad of Florisil. The filtrate was concentrated in vacuo and purified by GPC to give the corresponding ester **5**.

3.7. Spectral data for cage esters **5**

3.7.1. Cyclohex-2-enyl 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-carboxylate (**5b**)

Colorless solid. M.p.: 97 °C. ^{1}H-NMR: δ −0.09 (s, 1H), 0.22 (s, 18H), 0.29 (s, 18H), 1.60–1.95 (m, 4H), 2.03 (m, 2H), 5.26 (m, 1H), 5.74 (m, 1H), 5.90 (m, 1H). ^{13}C-NMR: δ 1.8, 3.1, 3.3, 19.1, 24.8, 25.5, 28.8, 68.1, 126.6, 131.6, 173.9. ^{29}Si-NMR: δ −21.3, −19.8. IR: ν_{max} 2920, 2855, 1674, 1460, 1377, 1254, 1173, 972, 812, 665 cm^{-1}. FAB MS: *m/z* 501 [M^{+}+3], 500 [M^{+}+2], 499 [M^{+}+1], 498 [M^{+}], 418, 402, 330, 129, 73. FAB HRMS: Calc. for $C_{21}H_{46}O_2Si_6$: 498.2113. Found: 498.2122.

3.7.2. (*Z*)-Pent-2-enyl 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-carboxylate (**5c**)

Colorless solid. M.p.: 106 °C. ^{1}H-NMR: δ −0.09 (s, 1H), 0.22 (s, 18H), 0.28 (s, 18H), 0.99 (t, 3H, J = 7.6 Hz), 2.03–2.16 (m, 2H), 4.60 (t, 2H, J = 6.9 Hz), 5.50–5.56 (m, 1H), 5.56–5.62 (m, 1H). ^{13}C-NMR: δ 1.8, 3.2, 3.3, 14.1, 20.8, 25.6, 59.8, 123.4, 136.4, 174.2. ^{29}Si-NMR: δ −20.9, −19.2. IR: ν_{max} 2951, 2897, 1678, 1437, 1400, 1256, 1161, 1005, 970, 812, 723, 681 cm^{-1}. FAB LRMS: *m/z* 488 [M^{+}+2], 487 [M^{+}+1], 486 [M^{+}], 417, 401, 329, 305, 129, 73. FAB HRMS: Calc. for $C_{20}H_{47}O_2Si_6$ [M^{+}+1]: 487.2191. Found: 487.2178.

3.7.3. (*E*)-Pent-2-enyl 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-carboxylate (**5d**)

Colorless solid. M.p.: 134 °C. ^{1}H-NMR: δ −0.09 (s, 1H), 0.21 (s, 18H), 0.28 (s, 18H), 0.99 (t, 3H, J = 7.6 Hz), 2.00–2.10 (m, 2H), 4.49 (d, 2H, J = 6.9 Hz), 5.54–5.61 (m, 1H), 5.77–5.84 (m, 1H). ^{13}C-NMR: δ 1.8, 3.2, 3.3, 13.3, 25.3, 25.6, 65.1, 123.7, 137.9, 174.1. ^{29}Si-NMR: δ −20.9, −19.2. IR: ν_{max} 2925, 2897, 1682, 1458, 1375, 1254, 1167, 968, 812, 681, 665 cm^{-1}. FAB LRMS: *m/z* 488 [M^{+}+2], 487 [M^{+}+1], 486 [M^{+}], 417, 401, 373, 329, 305, 261, 129, 73. FAB HRMS: Calc. for $C_{20}H_{47}O_2Si_6$ [M^{+}+1]: 487.2191. Found: 487.2204.

3.7.4. Dodec-2-ynyl 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-carboxylate (**5e**)

Colorless solid. M.p.: 76 °C (dec.). ^{1}H-NMR: δ −0.09 (s, 1H), 0.21 (s, 18H), 0.29 (s, 18H), 0.86 (t, 3H, J = 6.4 Hz), 1.20–1.30 (m, 12H), 1.42–1.53 (m, 2H), 2.15–2.20 (m, 2H), 4.60–4.65 (m, 2H). ^{13}C-NMR: δ 1.7, 3.1, 3.2, 14.1, 18.7, 22.6, 28.4, 28.8, 29.2, 29.3, 29.5, 31.9, 52.0, 74.9, 86.8, 173.5. ^{29}Si-NMR: δ −21.4, −19.4. IR: ν_{max} 2987, 2955, 2361, 1659, 1256, 1196, 970, 876, 810, 667 cm^{-1}. FAB LRMS: *m/z* 586 [M^{+}+4], 585 [M^{+}+3], 584 [M^{+}+2], 583 [M^{+}+1], 567, 525, 489, 455, 261, 129, 73. FAB HRMS: Calc. for $C_{27}H_{59}O_2Si_6$ [M^{+}+1]: 583.3130. Found: 583.3134.

3.7.5. Octyl 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-carboxylate (**5f**)

Colorless solid. M.p.: 73.5–74.6 °C. ^{1}H-NMR: δ −0.09 (s, 1H), 0.22 (s, 18H), 0.28 (s, 18H), 0.88 (t, 3H, J = 6.9 Hz), 1.22–1.40 (m, 10H), 1.60–1.67 (m, 2H), 4.04 (t, 2H, J = 6.9 Hz). ^{13}C-NMR: δ 1.8, 3.2, 3.3, 14.1, 22.6, 25.6, 26.3, 29.1, 29.20, 29.22, 31.8, 64.5, 174.5. ^{29}Si-NMR: δ −20.9, −19.4. IR: ν_{max} 2926, 2855, 1682, 1256, 1169, 812, 681, 665 cm^{-1}. FAB LRMS: *m/z* 534 [M^{+}+4], 533 [M^{+}+3], 532 [M^{+}+2], 531 [M^{+}+1], 515, 417, 329, 129, 73, 57, 43. FAB HRMS: Calc. for $C_{23}H_{55}O_2Si_6$ [M^{+}+1]: 531.2818. Found: 531.2811.

*3.7.6. (S)-1-Phenylethyl 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-carboxylate (**5g**)*

Colorless solid. M.p.: 131 °C. ^{1}H-NMR: δ −0.10 (s, 1H), 0.2025/0.2071 (split) (s, 18H), 0.24 (s, 18H), 1.58 (d, 3H, $J = 6.4$ Hz), 5.89 (q, 1H, $J = 6.4$ Hz), 7.25–7.29 (m, 1H), 7.30–7.35 (m, 2H). 7.37–7.42 (m, 2H). ^{13}C-NMR: δ 1.75, 1.82, 3.1, 3.20, 3.28, 21.9, 25.5, 72.7, 127.0, 127.8, 128.3, 141.7, 175.5. ^{29}Si-NMR: δ −20.9, −19.2. IR: ν_{max} 2923, 2854, 1672, 1461, 1377, 1253, 1167, 1055, 812 cm^{-1}. FAB LRMS: *m/z* 525 [M$^+$+3], 524 [M$^+$+2], 523 [M$^+$+1], 417, 401, 329, 105, 73. FAB HRMS: Calc. for $C_{23}H_{47}O_2Si_6$ [M$^+$+1]: 523.2192. Found: 523.2180.

*3.7.7. Dicylohex-2-enyl 2,2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]-octane-1,4-dicarboxylate (**6b**)*

Colorless solid. M.p.: 157 °C. ^{1}H-NMR: δ 0.32 (s, 36H), 1.55–2.10 (m, 12H), 5,26 (m, 2H), 5.73 (m, 2H), 5.90 (m, 2H). ^{13}C-NMR: δ 1.8 19.1, 24.8, 28.8, 68.3, 126.4, 132.0, 173.6. ^{29}Si-NMR: δ −18.9. IR: ν_{max} 2928, 2860, 1672, 1394, 1254, 1163, 1022, 870, 812, 669 cm^{-1}. FAB LRMS: *m/z* 625 [M$^+$+3], 624 [M$^+$+2], 623 [M$^+$+1], 622 [M$^+$], 608, 525, 417, 401, 329, 73. FAB HRMS: Calc. for $C_{28}H_{54}O_4Si_6$: 622.2638. Found: 622.2634.

4. Summary

We have demonstrated that polysilacage acid in single crystals forms hydrogen-bonded dimers that consist of the same enantiomers and forms layers similar to smectic phase in liquid crystals. In addition, we have found that esterification of the polysilacage is achievable only under the Mitsunobu conditions with diisopropyl azodicarboxylate. These findings open a new way for exploration of novel liquid crystalline materials utilizing polysilacage moiety as a core fragment.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 200 333 for compound **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by Grant-in-Aids for COE Research on Elements Science, No. 12CE2005 and Scientific Research on Priority Areas (A) 'Exploitation of Multi-Element Cyclic Molecules' from Ministry of Education, Culture, Sports, Science, and Technology, Japan. The authors thank Prof. Susumu Kitagawa and Dr Mitsuru Kondo of Kyoto University for X-ray analysis.

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