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Cholesteric Silatranes

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Most liquid crystals with a C_3 symmetry have so far been discotic systems, e.g., triphenylenes. In the context of calamitic systems research has concentrated on triptycenes and to a lesser extend on silatranes. In this contribution we report our investigations of cholesteric silatrane systems, which have been obtained by connecting a tribenzylsilatrane core to cholesteric groups via alkyl and siloxane spacer groups.

Keywords: liquid crystal; silatrane; benzylsilatrane; cholesteric

INTRODUCTION

Shape anisotropy based on convex molecules is an important requirement in the design of novel thermotropic liquid crystals. Recent computer simulation studies have shown that the formation of low ordered liquid crystalline mesophases developed from non-convex anisotropic mesogens with an overall "fan shape" is possible [1,2]. Research using triptycenes or tribenzosilatranes functionalised with alkyl chains has demonstrated that such systems can exhibit mesomorphic behaviour, however usually highly ordered phase structures have been observed [3,4]. Extension of triptycene along one of the molecular axes has indicated that the formation of high free volume assemblies is possible [5]. This is very interesting from a technological point of view [6]. Tribenzosilatranes, which have a threefold symmetry, a strong internal dipole and which have the potential to be extended in a broadly similar manner as the reported triptycenes can functionalised with suitable mesogens via alkyl siloxane spacers and nematic phase behaviour has been observed [7]. In this contribution

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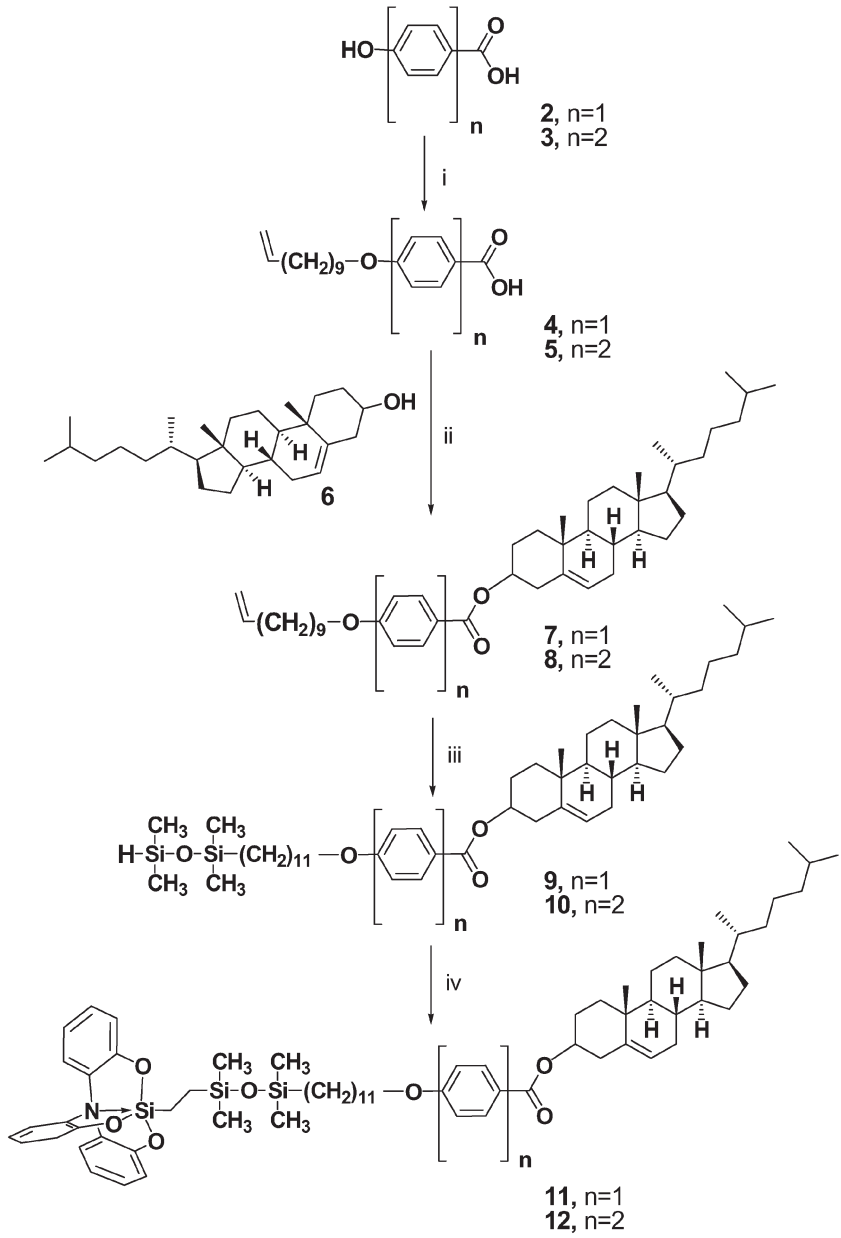

SCHEME 1 *Reagents and conditions*: i) 11-bromo-1-undecene, KOH, KI, water, ethanol; ii) cholesterol, DCC, DMAP, DCM; iii) tetramethyldisiloxane, Karstedt's catalyst, dry toluene; iv) vinyltribenzosiltrane **1**, Karstedt's catalyst, dry toluene.

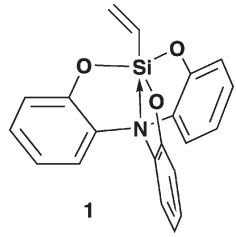

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FIGURE 1 Schematic structure of tribenzosilatrane **1**.

we report the results of our investigation of mesomorphic systems based on two tribenzosilatranes linked to chiral mesogens as it is shown in Scheme 1. Cholesteric groups were selected as the chiral mesogens. The tribenzosilatrane unit **1** shown in Figure 1 was selected as a model for a non-convex propeller shaped system, which exhibit three aromatic "blades" constituted by benzene rings interconnected via a nitrogen and a silicon-oxy function resulting in a large internal dipole moment. The free electron pair of the nitrogen atom is directed towards the apical silicon enabling the subsistence of a silicon with a fivefold functionality [8,9].

SYNTHESIS

The synthetic approach towards the nematic silatranes is convergent with the silatrane units and the rod shaped chiral groups being prepared separately and coupled in the last step. The synthesis of the tribenzosilatrane unit **1** follows broadly the literature reported methodology [10]. Compound **1** was obtained in a four step synthesis discussed in detail elsewhere [7].

The synthesis of two silatrane functionalised cholesterol derivatives **11** and **12** is shown in Scheme 1. Firstly, commercially available 4-hydroxybenzoic acid **2** and compound **3** were reacted with 11-bromo-1-undecene in the presence of potassium hydroxide and few crystals of potassium iodide in refluxing ethanol: water mixture furnishing compounds **4** and **5** respectively, after recrystallisation of the products from glacial acetic acid.

Cholesterol derivatives **7** and **8** were synthesised by coupling either compound **4** or compound **5** with commercially available cholesterol **6** via an esterification reaction using DCC and DMAP in dichloromethane as solvent to give materials **7** and **8** as white solids after purification by column chromatography. Compounds **7** and **8** were transformed in hydrosilylation reactions using 1,1,3,3 tetramethyldisiloxane to the siloxane functionalised materials **9** and **10**. These

compounds were reacted in the final step of the synthesis with tribenzosilatrane **1** under hydrosilylation reaction conditions to yield the final products **11** and **12** as white solids after purification by column chromatography. The chemical purity of the compounds was verified by spectroscopic methods. For the final products it should be noted that some β-addition to the vinyl groups of the benzyl silatrane unit took place when it was connected to the cholesteryl derivatives. This occurred in a yield of less than 5% of the total product and it could be detected in the ^{29}Si spectra of the final systems (signal at −20.63 ppm). However the by-products could not be removed by chromatographic methods or by recrystallisation techniques.

RESULTS

The synthesis of cholesterol derivatives **7** and **8** and their combination with tribenzosilatrane **1** has been successfully achieved yielding final products **11** and **12** respectively. The results of the calorimetric analysis (DSC) of the transitions, confirmed by optical polarising microscopy are shown in Table 1.

Cholesteryl derivatives **7** and **8** exhibit enantiotropic liquid crystal behaviour with isotropisation temperatures at 203°C (N*–Iso) for **7** and at 291°C (SmA–Iso) for **8**. The molecular structure of **8** contains an additional benzene ring compared to **7** resulting in a increase of about 90°C in the isotropisation temperature and the suppression of the N* phase exhibited by its analogue, material **7**.

The enthalpy associated with the transitions to the isotropic state are in the same range, 1.65 J/g for **7** and 1.19 J/g for **8**. This is unusual, as the SmA phase is higher ordered than the N* phase. However, comparing the reduced molar transition entropies $(\Delta S_{mol/R}) = (\Delta H_{mol/RT})$ with values of 0.29 for **7** and 0.19 for **8** it is observed that this effect is partly due to the large difference in the

TABLE 1 Transition Temperatures as Determined by DSC[a]

Comp	Transition temperatures (T/°C) (ΔH = J/g; ΔCp = J/g°C)
7	Cr 99 SmA 172 (0.66) N* 203 (1.65) Iso
8	Cr 95 SmA 291(1.19) Iso
11	Tg 25 (0.21) SmC* (0.45) 60 N* 72 (2.63) Iso
12	Cr 98 N* 164 (1.98) Iso

[a]ΔH = enthalpy of the transition, ΔCp = heat capacity of glass transition, Cr = crystalline, SmC* = chiral smectic C, SmA = smectic A, N* = chiral nematic, Iso = isotropic liquid, Tg = glass transition temperature; Comp = compound.

transition temperatures in these two systems in their different phases. In the final reaction step the benzyl silatrane molecule **1** was appended to mesogens **9** and **10** furnishing **11** and **12** respectively, which exhibit enantiotropic mesomorphism. Material **11** exhibits SmC^* ($\Delta H = 0.45\,J/g$) and N^* phase behaviour up to 72°C, where the compound clears to the isotropic with an associated enthalpy $\Delta H = 2.63\,J/g$. Material **12** exhibits only one mesophase. It clears at 164°C from the cholesteric phase to the isotropic and the enthalpy associated to this transition was $1.98\,J/g$. Notable is the presence of a glass transition observed for **11** ($\Delta Cp = 0.21\,J/g°C$) and the lack of crystalline phases. Nevertheless, material **12** has a similar structure as the analogue **11** and exhibits a low temperature crystalline state with melting point at 98°C.

CONCLUSION

The functionalisation of a tribenzosilatrane unit at the apex silicon with a vinyl group allows for the attachment of cholesteryl groups via siloxane and alkyl spacer units. The connection of tribenzosilatrane moieties to cholesteryl derivatives leads to the formation of chiral phases. SmC^* and N^* mesophase behaviour have been detected for the tribenzosilatrane functionalised cholesteric mesogens. To the best of our knowledge these materials are the first silatranes which form chiral mesophases. Compared to the non-substituted analogues, the silatrane functionalised systems exhibit transition temperatures which are considerably lower, reduced by about 150°C than what has been observed in the non-substituted derivatives. Noticeable is that phase sequence and phase structures can be altered when compared to non-substituted cholesteryl derivatives.

EXPERIMENTAL

All materials and solvents were used as purchased unless mentioned otherwise. Column chromatography was performed on silica gel (Fluorochem, 35–70 μ, 60 A). The purity of the synthesis products was checked by Thin Layer Chromatography (TLC) using silica gel 60 F254 (Merck) plates and subsequent detection was performed by UV fluorescence (254 nm). ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL Lambda 400 spectrometer (400, 100 and 55 MHz, respectively, for ^1H, ^{13}C and ^{29}Si) using tetramethysilane as internal standard. Chemicals shifts are given in ppm. Elemental analyses were carried out with a Fisons EA 1108 CHN analyzer. Transition temperatures were measured with a Mettler FP52 heating stage and FP5 control unit in conjunction

with an Olympus BH2 polarizing microscope and were confirmed with DSC measurements (Perkin-Elmer DSC 7, indium as standard).

Compound 4

Commercially available 4-hydroxybenzoic acid **2** (2.00 g, 14.5 mmol) was dissolved in hot ethanol (75 ml) and water (5 ml) together with potassium hydroxide (2.03 g, 0.036 mol) and few crystals of potassium iodide in a 250 ml three necked round bottom flask equipped with reflux condenser and magnetic stirrer. Afterwards 11-bromo-1-undecene (5.06 g, 21.7 mmol) was added and the mixture was refluxed for 24 hours. After this time a solution of potassium hydroxide (10%) in 70% ethanol was added to hydrolyse any ester formed and refluxing was continued for an additional 3 hours. Then, the solution was allowed to cool down to room temperature and finally acidified with concentrated hydrochloric acid until acid pH, giving a white solid. Recrystallisation of the solid from glacial acetic acid gave the desired product as a white powder (2.15 g, 51.13%); ^{1}H NMR (DMSO) δ: 1.30 (12H, m), 1.78 (2H, qui), 2.02 (2H, q), 4.01 (2H, t), 4.92 (2H, m), 5.77 (1H, m), 6.92 (2H, d), 8.0 4(2H, d); ^{13}C NMR (DMSO) δ: 25.95, 28.89, 29.05, 29.09, 29.31, 29.39, 29.47, 33.79, 68.25, 114.17, 121.16, 132.31, 139.22, 163.52, 171.30; Anal: $C_{18}H_{26}O_3$(290.40); Calc C: 74.45, H: 9.02%; Found C:74.47, H: 9.19%; MS (m/z): 290 $(M)^+$, 279, 214, 197, 167, 149, 138, 121, 97, 78, 69, 55 (100%).

Compound 5

Same procedure as described for compound **4**. Compound **3** (1.00 g, 4.67 mmol), 11-bromo-1-undecene (2.18 g, 9.35 mmol). Recrystallisation of the solid from glacial acetic acid gave the desired material as a white powder (1.26 g, 74%); $R_F = 0.39$ [CH_2Cl_2:ether (60:1)]; ^{1}H NMR (DMSO) δ: 1.21–1.41 (12H, m), 1.70 (2H, qui), 1.99 (2H, q), 3.99 (2H, t), 4.95 (2H, m), 5.76 (1H, m), 7.01 (2H, d), 7.65 (2H, d), 7.74 (2H, d), 7.95 (2H, d); ^{13}C NMR (DMSO) δ: 26.01, 29.05, 29.24, 29.54, 29.64, 34.09, 68.13, 116.03, 125.80, 128.35, 128.62, 129.75, 130.09, 144.49, 158.12, 167.35; Anal: $C_{24}H_{30}O_3$(366.50); Calc C: 78.65, H: 8.25%; Found C: 77.63, H: 8.53%; MS (m/z): 366 $(M)^+$, 214 (100%), 197, 185, 169, 152, 141, 115, 97, 83, 69.

Compound 7

A mixture of compound **4** (0.43 g, 1.48 mmol), cholesterol (0.69 g, 1.78 mmol), 4-dimethylaminopyridine (100 mg) and *p*-toluensulponic acid (50 mg) was dissolved in 40 ml of dichloromethane. The stirred

mixture was cooled to 0°C and addition of N,N′-dicyclohexylcarbodiimide (0.93 g, 4.5 mmol) to the reaction mixture was carried out. After five minutes stirring at 0°C the temperature was allowed to rise to room temperature and stirring was continued for 20 hours. Solid urea (white solid) was filtered off and the filtrate was evaporated to dryness. Purification of the solid residue was carried out by column chromatography using a gradient mixture of dichloromethane-hexane as eluent giving the desired product as a white solid (0.720 g, 74%); $R_F = 0.29$ [CH_2Cl_2:hexane (1:1)]; ^{1}H NMR ($CDCl_3$) δ: 0.69 (3H, s), 0.85–2.08 (54H, m), 2.44 (2H, d), 3.98 (2H, t), 4.79 (1H, m), 4.91 (2H, m), 5.40 (1H, d), 5.78 (1H, m), 6.88 (2H, d), 7.97 (2H, d); ^{13}C NMR ($CDCl_3$) δ: 14.70, 21.55, 22.22, 23.88, 25.40, 25.66, 26.66, 27.13, 28.80, 30.77, 30.85, 31.08, 31.74, 31.94, 32.17, 32.24, 32.32, 34.71, 34.77, 36.63, 38.63, 39.02, 39.49, 39.89, 41.12, 42.35, 45.15, 52.87, 58.96, 59.53, 71.00, 77.00, 116.78, 116.98, 125.49, 125.82, 134.33, 142.03, 142.62, 165.64, 168.65; Anal: $C_{45}H_{70}O_3$(659.035); Calc C: 82.01, H: 10.71%; Found C: 82.10, H: 11.00%; MS (m/z): 659 (M^+), 368 (100%), 353, 318, 247, 213, 195, 147, 121, 95, 55.

Compound 8

Same procedure as described for compound **7**. Compound **5** (0.20 g, 0.54 mmol), cholesterol (0.42 g, 1.09 mmol), N,N′-diciclohexylcarbodiimide (0.34 g, 1.64 mmol). The desired product was obtained as a white solid after purification by column chromatography (0.310 g, 77%); $R_F = 0.64$ (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ: 0.66 (3H, s), 0.83–1.65 (45H, m), 1.67–2.07 (9H, m), 2.43 (2H, d), 3.97 (2H, t), 4.81 (1H, m), 4.91 (2H, m), 5.41 (1H, d), 5.76 (1H, m), 6.95 (2H, d), 7.52 (4H, m), 8.05 (2H, d); ^{13}C NMR ($CDCl_3$) δ: 11.82, 18.69, 19.34, 21.02, 22.54, 22.80, 23.83, 24.25, 26.00, 27.88, 27.98, 28.21, 28.89, 29.08, 29.22, 29.35, 29.40, 29.49, 31.83, 31.89, 33.77, 35.78, 36.15, 36.60, 37.00, 38.22, 39.48, 39.70, 42.26, 50.00, 56.10, 56.64, 68.04, 74.44, 114.11, 114.83, 122.70, 126.25, 128.23, 128.79, 130.00, 132.15, 139.13, 139.63, 145.01, 159.33, 165.87; Anal: $C_{51}H_{74}O_3$(735.14); Calc C: 83.32, H: 10.15%; Found C: 83.58, H: 10.37%; MS (m/z): 735 $(M)^+$, 663, 484, 454, 424, 368, 366 (100%), 247, 214, 197, 162, 145, 121, 55.

Compound 9

To a stirred solution of compound **7** (0.4 g, 0.607 mmol) and 1,1,3,3-tetramethyldisiloxane (1.63 g, 0.012 mol) in 15 ml of dry toluene was added Karstedt's catalyst [platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex, 25 μl, 5% xilene]. The mixture was aerated

for a couple of minutes using a glass pipette in order to activate the catalyst. After stirring for 2 h the reaction at room temperature the solvent was removed under reduced pressure and the residue was purified by column chromatography using dichloromethane-hexane gradient mixture to obtain the desired compound **9** as a white solid which was reacted in the next step without further purification or analysis (0.430 g, 89%); $R_F = 0.33$ [CH_2Cl_2:hexane(1:1)].

Compound 10

Compound **10** was synthesised following the same procedure described for compound **9**. Compound **8** (0.17 g, 0.23 mmol) and 1, 1, 3, 3-tetramethyldisiloxane (0.93 g, 6.93 mmol). The desired product was obtained as a white solid after purification by column chromatography using hexane-dicholoromethane gradient mixture as eluent and it was employed in the following synthetic step without further analysis or purification (0.160 g, 80%); $R_F = 0.67$ (CH_2Cl_2).

Compound 11

The above mentioned material was synthesised following a similar procedure as described for the synthesis of compound **9**. Compound **9** (0.160 g, 0.202 mmol), compound **1** (0.070 g, 0.202 mmol). Reaction time 20 h. Purification was carried out by column chromatography using a hexane-dichloromethane gradient mixture as eluent to yield the desired product as a white solid (0.055 g, 24%); $R_F = 0.12$ [CH_2Cl_2):hexane (1:2)]; ^{1}H NMR ($CDCl_3$) δ: 0.00 (6H, s), 0,04 (6H, s), 0.44 (2H, t). 0.58 (3H, s), 0.74–1.95 (60H, m), 2.34 (2H, d), 3.85 (2H, t), 4.69 (1H, m), 5.30 (1H, d), 6.77 (2H, d), 6.80 (3H, m), 6.88 (3H, m), 7.00 (3H, m), 7.62 (3H, dd), 7.87 (2H, d); ^{13}C NMR ($CDCl_3$) δ: −0.14, 0.46, 5.23, 10.37, 11.84, 18.45, 18.70, 19.37, 21.03, 22.55, 22.82, 23.35, 23.81, 24.28, 25.93, 27.92, 28.00, 28.22, 29.09, 29.34, 29.41, 29.54, 29.59, 31.86, 31.91, 33.47, 35.78, 36.17, 36.63, 37.03, 38.27, 39.50, 39.72, 42.29, 50.01, 56.10, 56.67, 68.16, 74.14, 113.93, 117.76, 121.83, 122.64, 122.93, 126.57, 128.82, 131.48, 136.59, 139.76, 153.77, 162.80, 165.81; ^{29}Si NMR DEPT ($CDCl_3$) δ: −57.67, −20.64, 7.92, 9.08; Anal: $C_{69}H_{99}NO_7Si_3$(1138.78); Calc C: 72.77, H: 8.76, N: 1.23%; Found C: 72.65, H: 8.87, N: 1.21%; MS (m/z) MALDI-TOF: 1161.28 $(M + Na)^+$.

Compound 12

The target material was synthesised following a procedure described for the synthesis of compound **11**. Compound **10** (0.160 g, 0.184 mmol), compound **1** (0.190 g, 0.552 mmol). Reaction time 20 h. Purification of

the final residue was carried out by column chromatography using a gradient mixture of hexane-dichloromethane as eluent to give the desired product as a white solid (0.146 g, 65%); $R_F = 0.82$ (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ: 0.01 (6H, s), 0.05 (6H, s), 0.47 (2H, t), 0.60 (3H, s), 0.76–1.95 (60H, m), 2.38 (2H, d), 3.87 (2H, t), 4.74 (1H, m), 5.33 (1H, d), 6.81–6.92 (8H, m), 7.00 (3H, m), 7.45 (2H, d), 7.51 (2H, d), 7.64 (3H, dd), 7.97 (2H, d); ^{13}C NMR ($CDCl_3$) δ: −0.15, 0.46, 5.23, 10.36, 11.84, 14.12, 18.45, 18.70, 19.37, 21.02, 22.55, 22.64, 22.82, 23.35, 23.81, 24.27, 26.00, 27.89, 28.00, 28.23, 29.38, 29.43, 29.57, 29.60, 31.58, 31.85, 31.92, 33.48, 35.78, 36.16, 36.63, 37.02, 38.23, 39.50, 39.71, 42.29, 50.01, 56.10, 56.66, 68.09, 74.48, 114.87, 117.75, 121.83, 122.74, 126.32, 126.56, 128.27, 128.82, 130.03, 132.18, 136.58, 139.67, 145.07, 153.77, 159.37, 165.95; ^{29}Si NMR DEPT ($CDCl_3$) δ: −57.67, −20.63, 7.95, 9.08; Anal: $C_{75}H_{103}NO_7Si_3$ (1214.88); Calc C: 74.15, H: 8.55, N: 1.15%; Found C: 74.37, H: 8.84, N: 1.17%; MS (m/z) MALDI-TOF: 1237.88 $(M + Na)^+$.

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