A Polar Globular Mesogen: Synthesis of a Tetrasubstituted Tribenzosilatrane

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A tribenzosilatrane substituted with four alkyl tails has been synthesized in eight steps starting from *p*-alkylaniline with an overall yield of approximately 10%; this molecular unit is designed for fabricating a new type of material where the overall globular shape can facilitate the obtainment of cubic symmetry mesophases; the use of different side chains could also yield macrochiral centres.

Molecular materials are constructed of molecular units which can be subsequently organised into condensed phases.[1] This publication is devoted to the design of a chemical pathway which can lead to tetrasubstituted tribenzosilatranes (Fig. 1).

Substituted tribenzosilatranes represent a new type of unit for molecular materials with at least three original characteristics: (*i*) three benzene subunits are interconnected in a C_{3v} symmetry[2] to form the rigid core of the molecule, (*ii*) a large dipole moment (of the order of 4–9 D), due to a donor–acceptor interaction between the nitrogen and silicon atoms, is 'buried' within the cage-like structure of the molecular unit and (*iii*) the possibility of different substitution on the benzene rings and on the silicon atom permits us to envisage the generation of tetrahedral macrochiral species.

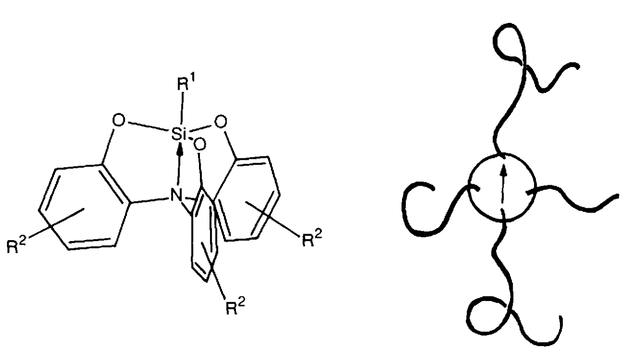

Fig. 1 Chemical formula and simplified representation of tetrasubstituted tribenzosilatranes (the arrow denotes the molecular dipole moment) ($R^1 = C_8H_{17}$, $R^2 = C_{12}H_{25}$: compound **6**)

The tetrasubstituted tribenzosilatrane **6** is synthesized from commercially available *p*-dodecylaniline, which is first transformed into 4-dodecyl-2-nitroanisole **1** in three chemical steps.[3–5] Compound **1** may also be obtained by following another chemical route.[6] *p*-Dodecylphenol (m.p. 65 °C) is obtained from the corresponding aniline by treatment with $NaNO_2$ (yield: 40%). Nitration with a mixture of $NaNO_3$–HCl (aq) leads to 4-dodecyl-2-nitrophenol (m.p. 54 °C) in 82% yield; compound **1** (m.p. 51 °C) is then obtained by treatment with MeI–K_2CO_3 in dimethylformamide (yield: 97%).

Compounds **2**–**6** are not mentioned in the literature (Scheme 1). The reduction of **1** into 4-dodecylanisidine **2** (m.p. 38.5 °C) is achieved with $NaBH_4$ catalysed with $Cu(acac)_2$[7] (quantitative yield) (Hacac = pentane-2,4-dione). The corresponding iodo-compound **3** (m.p. 33 °C) is obtained by diazotation in the presence of KI[8] (yield: 76%). Compounds **2** and **3** are treated in *o*-dichlorobenzene with copper leading to **4** (m.p. 12.5 °C) in 90% yield.[9,10] Demethylation is carried out with $AlCl_3$ in toluene[9] (yield: 85%) giving **5** (viscous oil) which is then treated with $C_8H_{17}SiCl_3$ in dibutyl ether[9] to give **6** in 52% yield.†

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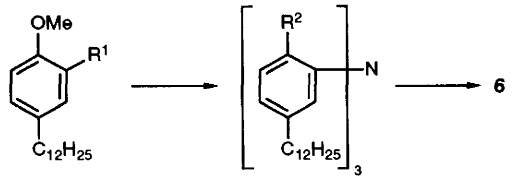
† MS (EI) *m*/*z* (%) 935.8 (20) [M^+], 822.6 (100) [$M^+ - C_8H_{17}$]. ^1H NMR ($CDCl_3$, $SiMe_4$): δ 7.45 (3H, s, Ar), 6.85 (6H, s, Ar), 2.45 (6H, t, $ArCH_2$), 1.25–0.80 (86H, m, $3 \times C_{11}H_{23} + C_8H_{17}$).



1; $R^1 = NO_2$
2; $R^1 = NH_2$
3; $R^1 = I$

4; $R^2 = OMe$
5; $R^2 = OH$

Scheme 1

The molecular dipole of **6** has been measured in benzene (μ_g = 4.9 D) and in $CHCl_3$ (μ_g = 4.6 D) using the Osipov's relationship[11] to interpret the experimental results.

Differential scanning calorimetry (DSC) studies have been carried out on **6**. A peak at 64.6 °C with a shoulder at 60 °C (ΔH = 95.2 J g^{-1} for the two peaks) is observed. Large supercooling is noticed (0.75 °C; ΔH = −28.7 J g^{-1}). By adding a small amount of decane (1% m/m), the DSC curves are importantly modified: four peaks appear at 15.4 °C (ΔH = 85 J g^{-1}), 39.7 °C (ΔH = 8.5 J g^{-1}) and 63.4–65.8 °C (ΔH = 6.7 J g^{-1}).

X-Ray measurements at small angles show that **6** forms spontaneously slightly orientated mesophases at room temp. and 60 °C. In the first case a body-centred cubic lattice is observed (a = 27.51 Å) and in the second case the X-ray pattern can be fitted (more than 15 peaks) to the face-centred cubic space group $F4_132$ (a = 25.77 Å). Preliminary density measurements indicate that two (or less probably three) molecules are associated to form the building units.

The tetrasubstituted tribenzosilatrane described in the present publication is the first compound of a series of products leading to original mesogens. The same chemical pathway may be used to synthesise macrochiral centres by adding four different substituents on the tribenzosilatrane core. Such studies are in progress.

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