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Separation and identification of stereoisomers of a tetrameric side-chain liquid crystalline cyclic siloxane

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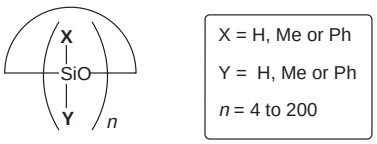
For the first time the four stereoisomers of a tetrameric side-chain liquid crystalline cyclic siloxane have been isolated in a pure state by high performance liquid chromatography. The structure of one of the stereoisomers was confirmed by ^{1}H, ^{13}C and ^{29}Si NMR. The structures of the remaining three stereoisomers were assigned by using evidence from the literature and their liquid crystalline thermal properties. All four stereoisomers and the isomeric mixture exhibited calamitic SmC and SmA phases; no discotic phases were found.

Introduction

The synthesis of cyclic polysiloxanes of structure **1** has been carried out for a number of years resulting in a wide range of cyclic materials being prepared, some of which are now commercially available.



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Most research has been undertaken on the methylphenylcyclosiloxanes (structure **1**, X = Me, Y = Ph) and the dimethylcyclosiloxanes (structure **1**, X = Y = Me) due to the fact that they form stable cyclic polymers. Research work has also been carried out into the different isomeric forms of these materials.[1,2] When the cyclic siloxane backbone is synthesised, it is possible to form a number of different stereoisomers for each ring system. If we take, for example, the tetramethyltetraphenylcyclosiloxane ring, it can be shown that there are four stereoisomers formed in the preparation of the cyclic tetramer.[3] These stereoisomers are formed because at each silicon atom it is possible to have a substituent in one of two possible spatial positions. Upon formation of the rings, as the silane molecules interact, the spatial arrangement of the substituents on the silicon atom governs the final arrangement when the ring closes.

After the ring has closed and formed, the arrangement of the substituent groups is effectively fixed. The ring can undergo the usual translational and vibrational motions, but unless the ring is cleaved by thermal or chemical methods, the spatial arrangement at each silicon atom will remain unchanged. It is this 'randomness' of interaction of the silane molecules that gives rise to the isomeric forms for the cyclic siloxanes.

The cyclic siloxanes that are of interest today are not disubstituted siloxanes, but are in fact the methylhydrogencyclosiloxanes (structure **1**, X = Me and Y = H), which can be used in coatings, inks and adhesive technologies.[4]

In recent years the ability of these cyclic siloxanes to react with an alkenic group attached to a mesogenic side chain has led to the preparation of a wide range of side-chain liquid crystalline polymers.[5–9] This hydrosilylation reaction is shown in Fig. 1.

Like the methylphenylcyclosiloxanes, side-chain liquid crystalline (SCLC) siloxanes of structure **2** (Fig. 1), based on the cyclic tetramer (structure **2**, $n = 4$) and pentamer (structure **2**, $n = 5$), can also give rise to four stereoisomers. A schematic representation of the four stereoisomers for a SCLC cyclic tetramer is given in Fig. 2.

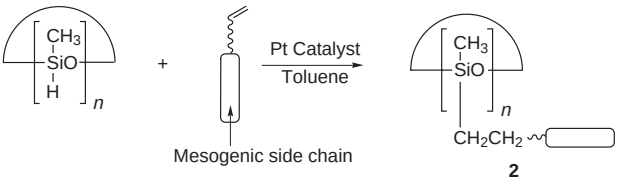

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Fig. 1 The hydrosilylation reaction.

Although a substantial number of side-chain liquid crystalline cyclic siloxanes of general structure **2** have been prepared from the tetramethyltetrahydrogensiloxane cyclic backbone, no attempt has ever been made to separate and evaluate the effect of each of the individual isomers on the thermal and physical properties of the isomeric mixture.

In this paper we detail, for the first time, the separation, characterisation and thermal properties of the four stereoisomers of a SCLC cyclic tetramer.

Results and discussion

A number of structure–property correlation studies have been carried out on cyclic SCLC siloxanes, to investigate the role of molecular structure of (a) the polymer backbone, (b) the

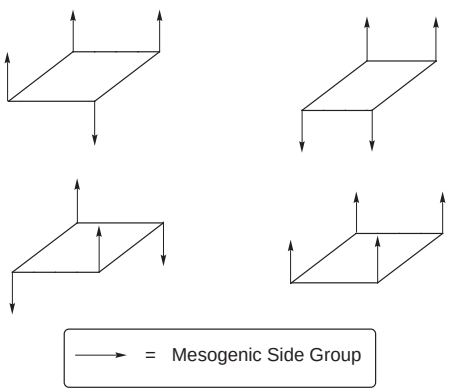


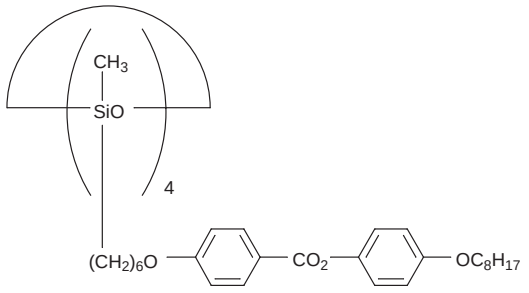
Fig. 2 Representation of the four stereoisomers for a SCLC cyclic tetramer.

spacer group and (c) the mesogenic side chain, on the thermal and physical properties of the polymer. However, the separation of the stereoisomers of a SCLC cyclic siloxane has never been attempted and therefore it is not known how each individual isomer contributes to the overall thermal properties of the mixture. The existence of a discotic phase for these types of materials has been predicted by molecular modelling using the Monte Carlo technique.[10,11] Further calculations undertaken using different computer molecular modelling programmes have also identified the possibility of the existence of a discotic-type mesophase for these cyclic siloxanes, although many of these studies do suggest that the formation of a calamitic mesophase is more likely.[12,13] A large number of SCLC cyclic siloxanes have been prepared incorporating a wide range of differing mesogenic side groups and spacer groups, but they *all* exhibit calamitic phases.

It is possible that the overall thermal properties of a SCLC cyclic siloxane is being dominated by just one of the stereoisomers which happens to exhibit a calamitic phase, and that one or more of the remaining stereoisomers are forming discotic phases. On the other hand it is also possible that the computer modelling of these systems, which predicts discotic phases, may be incorrect and that all the isomers are calamitic. The only way to answer these questions is to separate the individual isomers of a SCLC cyclic siloxane and to investigate their phase behaviour.

The separation of stereoisomers

The separation of the individual stereoisomers of the SCLC cyclic siloxanes of structure **3** was carried out using high performance liquid chromatography (HPLC). Details of the preparation of the cyclic tetramer of structure **3** and a detailed description of the HPLC equipment and procedures used to separate the four stereoisomers are given in the Experimental section.



K_1 78.4 K_2 86.0 SmC 103.6 SmA 108.8 °C Iso

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Using our HPLC assembly and data handling software, we were able to determine the percentages of the individual stereoisomers in the isomeric mixture and this information is given in Table 1. These results clearly show the presence of four stereoisomers for the SCLC cyclic siloxane studied and that one isomer, isomer 3, constitutes over half the composition of the isomeric mixture. Although it is possible to separate these isomers by preparative HPLC, our earlier studies have shown that the separation of isomers 1, 2 and 3 (especially isomers 1 and 2) will be difficult. Indeed, this proved to be the case. After many pilot studies the separation of isomer 4 was achieved with relatively little difficulty using our preparative isocratic HPLC systems. However, sample preparation of the 3 remaining isomers proved problematic because the removal of isomer 4 from the isomeric mixture led to a dramatic change in the solubility of the 3 remaining isomers in the chloroform–acetonitrile mixture, a mixture that was used as the mobile phase in our HPLC systems. Because of the solubility problem and the close proximity of isomer 3 to isomers 1 and 2 in the HPLC chromatogram, it was found necessary to change the HPLC system to a preparative gradient HPLC system. By using a 'cut-off' method, isomer 3 was separated.

Table 1 The percentages of the four stereoisomers in the LC isomeric mixture

Isomer number	% Isomer in mixture
1	13
2	28
3	53
4	6

The separation of the remaining two isomers was very difficult and a number of studies using analytical HPLC had to be carried out to obtain the best conditions for separation. It was found necessary to use both our 'cut-off' method and a column oven, set at a temperature of 30 °C, to achieve the separation.

A detailed description of the procedures used to carry out the separation of the stereoisomers is given in the Experimental section.

Confirmation of structure and thermal properties of isomers

The separation of the four isomers was only the first part of this investigation. The next step was to identify the structure of the stereoisomers and examine their liquid crystalline behaviour.

All the following NMR spectra were carried out by Professor J. W. Emsley at the University of Southampton. The transition temperatures and phase identification were carried out at Hull using DSC and optical light microscopy. When necessary X-ray diffraction was used to identify the phases and this was carried out by Dr R. M. Richardson at the University of Bristol.

The structure of stereoisomer 3 was confirmed by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. Stereoisomers 1, 2 and 4 all showed similar ^{1}H, ^{13}C and ^{29}Si NMR spectra due to the symmetry of the mesogenic side groups and therefore, such data could not be used to elucidate the structure of these three stereoisomers. The structures of stereoisomers 1, 2 and 4 were tentatively assigned using evidence from the literature and their liquid crystalline behaviour.

Stereoisomer 3

The separation of this isomer was regarded as very important, because a knowledge of the phase behaviour of this isomer would give some indication as to the factors that influence the phase behaviour of the bulk material. This isomer accounts for 53% of the total composition of the isomeric mixture (see Table 1).

The structure of the pure stereoisomer 3 was confirmed using ^{1}H, ^{13}C and ^{29}Si NMR. The NMR spectra for stereoisomer 3 are shown in Fig. 3 (^{29}Si), 4 (^{13}C) and 5 (^{1}H), and it is the only stereoisomer where the NMR data are unambiguous regarding its structure.

The ^{29}Si NMR spectrum (Fig. 3) gave a clear indication as to the structure of stereoisomer 3 because there is only one structure that could lead to more than one type of silicon atom peak appearing in the NMR spectrum. A schematic representation of this arrangement of methyl and mesogenic side groups is shown in Fig. 6.

There are two silicon atoms, a and b in Fig. 6, which carry an axially positioned methyl group but the methyl groups on adjoining silicon atoms are *cis* (c) and *trans* (d). Thus the silicon atoms a and b have similar environments. In the case of the silicon atom c, although the methyl group is again axially positioned on the silicon atom, the adjoining methyl groups on silicon atoms a and b are both *cis*. This would

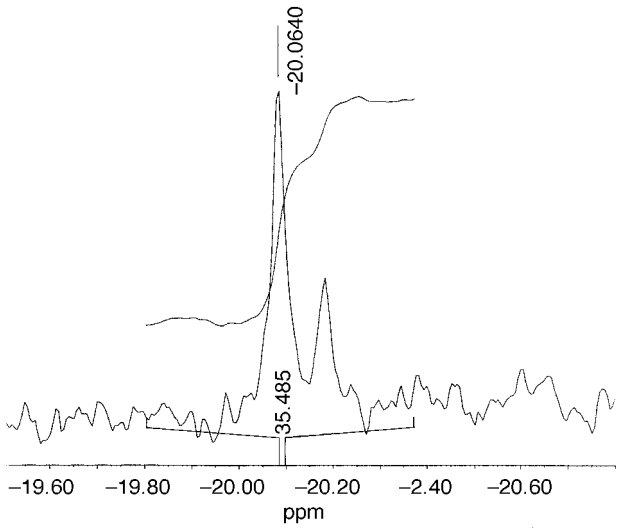


Fig. 3 The ^{29}Si NMR spectrum for stereoisomer 3.

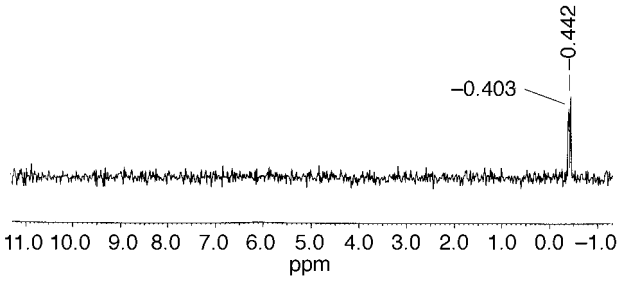


Fig. 4 The ^{13}C NMR spectrum for stereoisomer 3.

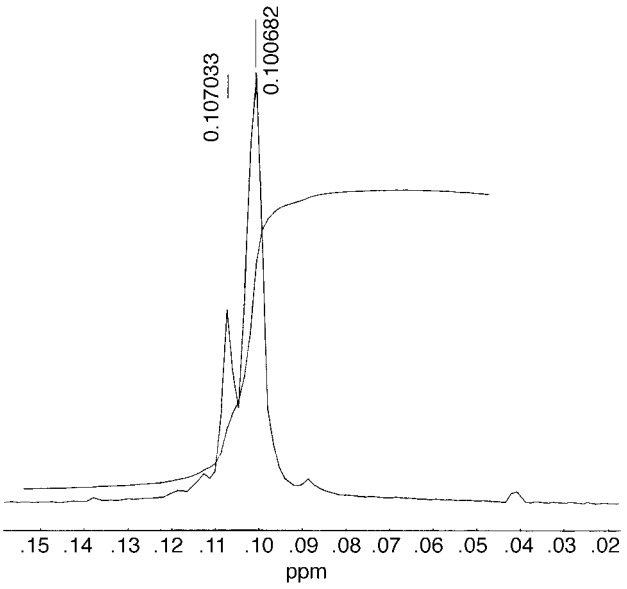


Fig. 5 The ^{1}H NMR spectrum for stereoisomer 3.

mean that silicon atom c has a very slightly different environment to that experienced by silicon atoms a or b. However, this subtle difference between the environments of silicon atom c and silicon atoms a and b could not be resolved by ^{29}Si NMR and therefore all three silicon atoms appear as a single peak in the spectrum at −20.08 ppm. In the case of the silicon atom d the methyl group is equatorially positioned and appears as a single peak at −20.18 ppm. The ratio of the two single peaks is 3 (−20.08) : 1 (−20.18).

Both the ^{13}C NMR spectrum (Fig. 4) and ^{1}H NMR spectrum (Fig. 5) support the strong structural evidence from

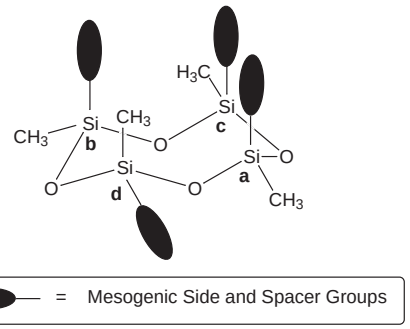


Fig. 6 Schematic representation of the structure for stereoisomer 3.

^{29}Si NMR that the structure of the stereoisomer 3 is that shown in Fig. 6; three of the mesogenic side groups are attached to the same plane of the ring backbone, the remaining mesogenic side group is attached to the opposite ring face.

The following transitions were found for isomer 3. The transitions in brackets are for the isomeric mixture.

K_1 80.0 K_2 86.5 SmC 108.8 SmA 111.7 °C Iso

(K_1 78.4 K_2 86.0 SmC 103.6 SmA 108.8 °C Iso)

The spatial arrangement of the four mesogenic side groups around the siloxane ring in stereoisomer 3 would cause the cyclic tetramer to adopt the calamitic 'bundle-type' configuration as shown in Fig. 7 (a). This would mean that the material would be unlikely to pack in a way that would lead to the formation of a discotic phase.

The transition temperatures for stereoisomer 3 differ only very slightly from those of the isomeric mixture. This was not unexpected since isomer 3 constitutes over half the isomeric mixture. The clearing point (SmA–Iso) and the SmC–SmA transition temperature are higher (2.9 and 5.2 °C respectively) for stereoisomer 3 than for the isomeric mixture.

Stereoisomers 1, 2 and 4

The ^{1}H, ^{13}C and ^{29}Si NMR spectra for these three stereoisomers were all identical and therefore such data could not be used to assign the configuration of stereoisomers 1, 2 and 4. To assign the configuration of these three stereoisomers, we used both evidence from the literature and their liquid crystalline behaviour.

From the work of Beevers and Semlyen[14] on the separation and identification of stereoisomers of cyclic tetramethyltetraphenylsiloxanes, they found that the amounts of the stereoisomers for undiluted and solution equilibrates of this cyclic tetramer, and the ratio of the stereoisomeric cyclics produced by the non-equilibrium pyrolysis reaction, were very close to the isomer ratio predicted from the random cyclisation of an atactic polysiloxane. These results are given in Table 2. The

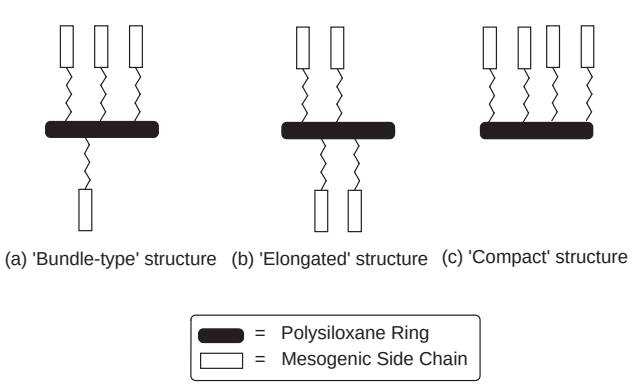


Fig. 7 Schematic representations for the different arrangements for the stereoisomers.

Table 2 The percentages of tetramers 1 to 4 in different isomeric mixtures

Stereoisomers, as defined in Fig. 8	% Stereoisomers in different mixtures			
		Equilibrate		
	Predicted	Undiluted	Solution	Pyrolysis
Tetramer 1	12.5	8.0	10.0	16.0
Tetramer 2	50.0	49.0	49.0	51.0
Tetramer 3	25.0	25.0	23.0	24.0
Tetramer 4	12.5	18.0	18.0	10.0

assignment of the configuration of the cyclic tetramers 1–4 from Table 2 are given in Fig. 8, and these were derived by Beevers and Semlyen.[14] If we now compare these results with those given in Table 1 for our cyclic SCLC tetramer, we can clearly see that tetramer 2 (Table 2, Fig. 8) has the same basic type of structure as stereoisomer 3 (Table 1, Fig. 6), and that both contribute half the composition of the isomeric mixture. This gave us strong evidence that, provided that all the Si–H sites on the cyclic tetramethyltetrahydrogensiloxane had been substituted by the mesogenic side chain, then the ratio of the stereoisomers in our cyclic SCLC tetramer mixture should be very similar to those for the cyclic methylphenylsiloxane tetramer mixture given in Table 2. The loss of the Si–H signal in the IR and the absence of any other peaks, except for the presence of the four stereoisomers, in the HPLC chromatogram for our cyclic SCLC tetramer (see Experimental section), showed that we had 100% substitution of the Si–H by the mesogenic side chain. Furthermore, some unpublished work by J. A. Semlyen, University of York, showed that the cyclic tetramethyltetrahydrogensiloxane used in this work was a random atactic cyclic polymer similar to the cyclic methylphenylsiloxane used in the work presented in Table 2. This enabled us to predict, with some certainty, that stereoisomer 2 has the same structure as tetramer 3, both contributing to about 25% of the composition of their respective isomeric mixtures.

The configuration of stereoisomers 1 and 4 could not be predicted from the information given in Table 2 since the relative ratios of tetramers 1 and 4 in Table 2 depended on equilibration and the mode of preparation, *i.e.* in column 2 of Table 2 (undiluted equilibrate) the percentage ratio of tetramer 1 : 2 in the isomeric mixture is 8 : 18, but in column 4 (preparation by pyrolysis) the ratio is 16 : 10. However, unlike previous work on cyclic siloxanes we can now use the liquid crystalline behaviour of our SCLC cyclic tetramers to try to predict the configuration of stereoisomers 1 and 4. This evidence will also substantiate that the configuration of stereoisomer 2 is that of tetramer 3 in Fig. 8.

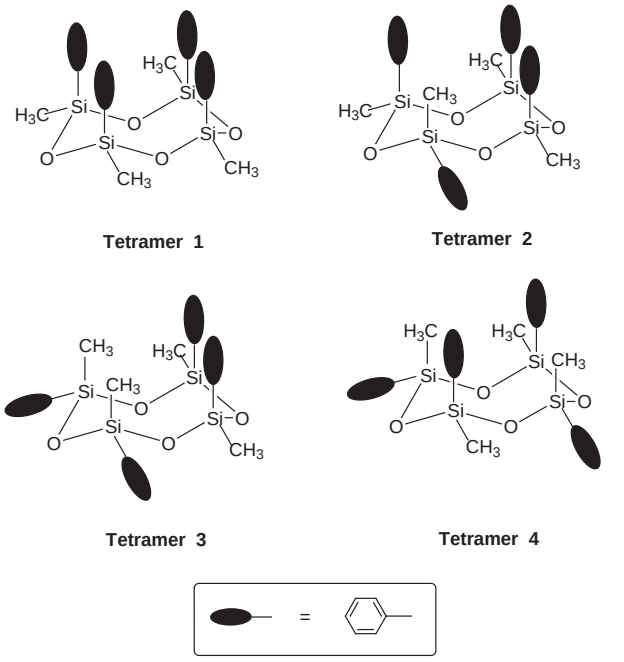


Fig. 8 The assignment of the configuration of cyclic tetramers 1–4 in Table 2.

Liquid crystalline behaviour of the stereoisomers

The liquid crystalline behaviour of the four stereoisomers for our SCLC cyclic tetramer are given in Table 3. The most important fact that comes out of the information given in Table 3 is that all the stereoisomers exhibit *calamitic* phases; no discotic phases. Whether this will be true for all SCLC cyclic siloxanes we cannot say, but in this case there was no evidence of discotic phases.

The more ordered phase S_1 found in stereoisomer 4 in Table 3 was originally identified by optical microscopy as a smectic B phase. X-Ray crystallography studies carried out by Dr R. M. Richardson at the University of Bristol proved that this was not the case. Although X-ray data confirm that there is a transition at 102.5 °C as shown by DSC (very small peak) and optical microscopy, the data clearly show that this is not a smectic C to smectic B transition but merely a subtle structure change from the normal SmC phase to a more highly ordered smectic C phase. The DSC data also confirm this fact in that the enthalpy for the transition is 1.58 J g^{-1}, which is smaller than would be expected for a smectic C to smectic B transition. The formation of this more ordered SmC phase is obviously due to the ability of the pure isomer to pack much more efficiently than the other three stereoisomers. This increase in ordering due to the packing of the mesogenic side groups is indicative of the structures given for tetramers 1 and 3 in Fig. 8, which would mean that stereoisomers 2 and 4 must have the configuration of tetramers 1 and 3, since both stereoisomers have high SmC and SmA thermal stabilities. This would mean that stereoisomer 1 must have the configuration of tetramer 4. In Fig. 8, if the black oblong shapes were mesogenic side chains and not benzene rings, then the more 'elongated' structure of tetramer 3, compared to the more 'compact' structure of tetramer 1 [see Fig. 7 (b) and (c)] would lead to this cyclic SCLC tetramer exhibiting the higher clearing point, but the spatial arrangement of the mesogenic side chains in tetramer 3 would also be more detrimental to the formation of crystal (K, K_1 and K_2) phases than that given for tetramer 1. Since stereoisomer 2 in Table 3 has only one crystal–crystal transition at 58.8 °C and this is considerably lower than the two crystal–crystal transitions given for stereoisomer 4, this led us to believe that stereoisomer 2 has the structure of tetramer 3 and stereoisomer 4 that of tetramer 1. The alternate spatial arrangement of the mesogenic side chains in tetramer 4 would be detrimental to the formation of crystal, SmC and SmA phases, and this was a good reason for us to believe that stereoisomer 1 has the structure of tetramer 4.

In the case of stereoisomers 1 and 2, where the mesogenic side groups are split evenly between the facial planes of the siloxane ring, these arrangements of the mesogenic side chains have manifested low crystal to SmC transitions, and this gives rise to very wide SmC ranges being exhibited by these two tetramers. It is interesting to note that these two stereoisomers also give the widest SmA ranges, wider than that observed for the isomeric mixture.

Conclusions

We have, for the first time, successfully separated and identified the stereoisomers of a SCLC cyclic siloxane. In the case of stereoisomer 3 the structure of the isomer was confirmed by

Table 3 The thermal data for the four stereoisomers and the LC isomeric mixture

	Transition temperature/°C								
Isomer	K_1–K_2	K_2–SmC	K_2–S_1	K–SmC	S_1–SmC	SmC–SmA	SmA–I	SmC range	SmA range
Mix	78.4	86.0				103.6	108.8	17.6	5.2
1	39.2	60.0				94.1	102.1	34.1	8.0
2				58.8		108.8	117.5	50.0	8.7
3	80.0	86.5				108.8	111.7	22.3	2.9
4	76.8		88.2		102.5	114.0	116.1	25.8[a]	2.1

[a]This range includes the S_1 phase range.

^{1}H, ^{13}C and ^{29}Si NMR but for stereoisomers 1, 2 and 4 their structures were deduced using evidence from the literature and their liquid crystalline behaviour. The configurations of the four stereoisomers of the cyclic tetramer and their corresponding transitions are given in Fig. 9.

Although a number of computer studies have predicted that these types of cyclic siloxanes should exhibit discotic phases, all four stereoisomers and the isomeric mixture gave calamitic SmC and SmA phases; no discotic phases were found. It is interesting to note that besides the ordered SmC phase exhibited by stereoisomer 4, all four stereoisomers gave the same liquid crystalline phase sequence as the isomeric mixture, *i.e.* SmC–SmA–Iso. No other phases were found for either the four stereoisomers or the isomeric mixture.

The structure of stereoisomer 4, where all four mesogenic side groups lie on the same face of the siloxane ring, is conducive to the formation of the SmC phase, whereas the 'two up, two down' arrangement of the mesogenic side chains (pairs of mesogenic side chains are split evenly between the two facial planes of the siloxane ring) in stereoisomer 2 is more conducive to the formation of the SmA phase. The alternating arrangement of the mesogenic side chains found in stereoisomer 1 is detrimental to the formation of both the SmC and SmA phases to such an extent that this is the only stereoisomer where the thermal stability of either the SmC or SmA phase is lower than that found for the isomeric mixture.

Experimental

Preparation of the SCLC cyclic polysiloxane

^{1}H Nuclear magnetic resonance spectroscopy (NMR) were carried out on a JMN GX270FT spectrometer, using deuterated chloroform as a solvent and tetramethylsilane as the internal standard. The peak types in the NMR spectra are denoted by the following notations: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m).

Infrared spectra were obtained using a Perkin Elmer 487G or a Perkin Elmer 983G spectrophotometer. Samples were prepared as either potassium bromide discs, or, if liquid, were run on single crystal sodium chloride discs.

Mass spectra were obtained using a Finigan Mat 1020 Automated GCMS Spectrometer. Results are quoted where M^+ represents the molecular ion and the base peak represented by (100%).

Differential Scanning Calorimetry (DSC) thermograms were obtained using a Perkin Elmer DSC 7, with a TAC 7/PC interface and a controlled cooling accessory. The heating rate was initially 20 °C min^{-1} and subsequent heating and cooling at 10 °C min^{-1}. Calculations were made using Perkin Elmer PC based software. The instrument was calibrated against an indium standard (melting temperature 156.6 °C, ΔH 28.45 J g^{-1}).

Optical microscopy was performed using an Olympus BH2 polarising microscope, fitted with a Mettler FP52 hot stage and a Mettler FP5 controller. Samples were prepared as thin films between a glass slide and a glass cover slip.

Column chromatography was carried out under flash chromatography conditions[12] unless stated otherwise. The stationary phase used was Sorbsil C60 (40–60 μm).

Analytical high performance liquid chromatography (HPLC) was carried out using a reversed phase HPLC column (25 × 0.46 cm, Dynamax, Microsorb, 5 μm C18 column) and a Spectroflow 757 UV detector (254 nm) with data handling facilities.

The compounds outlined in Scheme 1 have relatively simple structures and in our view the NMR, IR and MS data given are more than adequate to confirm the structure of these compounds. We believe that microanalysis would convey no additional information as to the structure of our compounds and, in this case, is not needed. 4-Octyloxyphenol is a known compound.[15]

The synthetic route to the preparation of the SCLC cyclic polymer is given in Scheme 1.

Preparation of 4-octyloxy-1-benzyloxybenzene

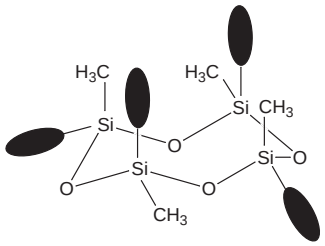
4-Benzyloxyphenol (10.00 g, 0.05 mol), 1-bromooctane (9.65 g, 0.05 mol), potassium carbonate (34.00 g, 0.25 mol) and potassium iodide (0.10 g) in dry butanone (100 ml) were heated under reflux, with stirring, overnight. The potassium salts were removed by filtration (Hyflo) and the solvent removed by distillation under reduced pressure. The crude ether was then purified by column chromatography on silica gel, eluting with dichloromethane, and the resultant product recrystallised (ethanol), to yield 4-octyloxy-1-benzyloxybenzene as a white crystalline solid (purity, 100% by HPLC). Yield = 12.30 g (79%), mp 97–98 °C. ^{1}H NMR ($CDCl_3$) δ 7.35 (4H, m), 6.85 (2H, m), 5.00 (2H, s), 3.90 (2H, t), 1.75 (2H, m), 1.35 (10H, m), 0.90 (3H, m). IR (KBr) ν_{max} 2960, 2940, 2920, 2860, 1510, 1250 cm^{-1}. MS *m/z* 312 (M+), 200, 109, 91 (100%).

Preparation of 4-octyloxyphenol

4-Octyloxy-1-benzyloxybenzene (10.00 g, 0.03 mol), cyclohexene (4.00 g, 0.05 mol) and 5% palladium on charcoal (0.2 g) in ethanol (100 ml) and glacial acetic acid (20 ml) were heated under reflux, with stirring, for 3 h. After filtration (Hyflo) the solvent was removed by distillation under reduced pressure. The crude phenol was purified by recrystallisation (ethanol) to yield 4-octyloxyphenol as a white powder (purity, >99% by HPLC). Yield = 5.80 g (88%), mp 61.0 °C (lit.,[15] 60.0–61.0 °C). ^{1}H NMR ($CDCl_3$) δ 7.40 (2H, m), 6.85 (2H, m), 5.00 (1H, s), 3.90 (3H, t), 1.75 (2H, m), 1.35 (10H, m), 0.90 (2H, m). IR (KBr) ν_{max} 3600–3250, 2960, 2930, 2920, 2860, 1510, 1240 cm^{-1}. MS *m/z* 222 (M+), 178, 167, 149, 136, 123, 110 (100%).

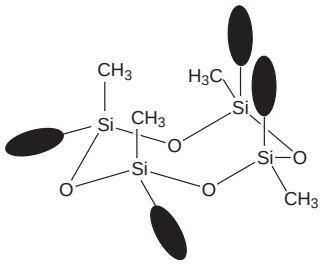
Preparation of 4-octyloxyphenyl 4′-(hex-5-enyloxyphenyl) benzoate

4-(Hex-5-enyloxy)benzoic acid (3.00 g, 10 mmol), 4-octyloxyphenol (2.70 g, 10 mmol) and dimethylaminopyridine (0.25 g, 1.2 mmol) were dissolved in dry dichloromethane (100 ml) under anhydrous conditions. *N*′,*N*-Dicyclohexylcarbodiimide (2.54 g, 10 mmol) in dry dichloromethane (15 ml) was added



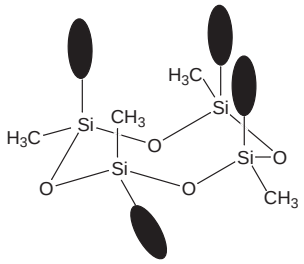
K_1 39.2 K_2 60.0 SmC 94.1 SmA 102.1 °C Iso

Stereoisomer 1



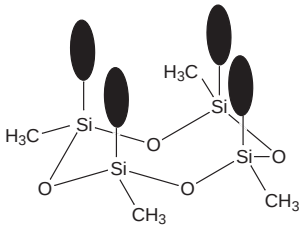
K_1 58.8 SmC 108.8 1 SmA 117.5 °C Iso

Stereoisomer 2



K_1 80.0 K_2 86.5 SmC 108.8 SmA 111.7 °C Iso

Stereoisomer 3



K_1 76.8 K_2 88.2 S_1 102.5 SmC 114.0 SmA 116.1 °C Iso

Stereoisomer 4

Fig. 9 Structure and transition temperatures for stereoisomers 1 to 4.

and the mixture allowed to stir overnight, at room temperature. Any undissolved material was filtered off and the solvent removed by distillation under reduced pressure. The crude ester was then purified by flash column chromatography (silica gel), eluting with a 2:1 mixture of dichloromethane–petroleum fraction (bp 40–60 °C) to yield 4-octyloxyphenyl 4′-(hex-5-enyloxyphenyl)benzoate as a white powder (purity, 100% by HPLC). Yield = 3.20 g (78%), transition temperatures K 25 SmC 44.6 SmA 74.6 °C Iso. ^{1}H NMR ($CDCl_3$) δ 8.15 (2H, d), 7.10 (2H, d), 6.95 (2H, d), 6.90 (2H, d), 5.85 (2H, m), 5.00 (1H, m), 4.05 (2H, t), 3.95 (2H, t), 2.15 (2H, m), 1.80 (4H, m), 1.6 (2H, m), 1.50–1.25 (10H, m), 0.90 (3H, t). IR (KBr) ν_{max} 3000–2840, 1720, 1600, 1500, 1260, 760 cm^{-1}. MS m/z 424 (M+), 312, 109, 91 (100%), 71, 57.

Preparation of SCLC cyclic tetramer

The cyclic tetramer backbone (0.25 g), 4-octyloxyphenyl 4′-(hex-5-enyloxyphenyl)benzoate (1.8 g) and Speiers catalyst (4–6 drops of a prepared solution) were dissolved in dry toluene (15 cm^3), and heated with stirring at 60 °C under anhydrous conditions for 24 h. The progress of the reaction was monitored using IR spectroscopy by examining the spectra in the region of 2155 cm^{-1} (Si–H fingerprint absorption). The disappearance of this band indicates completion of the hydrosilylation reaction.

Upon completion any undissolved material was filtered off and the toluene was removed by distillation under reduced pressure. The SCLC cyclic tetramer was reprecipitated by dissolving the tetramer in the minimum amount of dry dichloromethane and then excess dry methanol was added (at least four times the volume of the dichloromethane). The resultant suspension was then centrifuged at 4500 rpm for 30 min, the liquid was then decanted off. The process was repeated until TLC analysis (silica gel, 9:1 petroleum fraction (bp 40–60 °C)–diethyl ether) showed that the monomer had been removed.

The SCLC cyclic tetramer was then redissolved in dry dichloromethane and filtered through a disposable syringe filter (PTFE membrane 0.45 μm) to remove any particulates. The solvent was carefully removed by distillation under reduced pressure and the tetramer dried *in vacuo*. ^{1}H NMR ($CDCl_3$) δ 8.25 (2H, d), 7.15 (2H, d), 6.90 (2H, d), 6.85 (2H, d), 4.05 (2H, t), 3.95 (2H, t), 2.15 (2H, m), 1.80 (4H, m), 1.65 (2H, m), 1.10–1.50 (14H, m), 0.90 (3H, t), 0.05 (12H, m). IR (KBr) ν_{max} 3000–2840, 1950, 1875, 1850, 1720, 1605, 1560, 1280, 760 cm^{-1}.

A sample of the SCLC cyclic tetramer was sent to ICI Wilton for MALDI-TOF. The MALDI-TOF mass spectrometer was operated in the reflectron mode at a voltage of 29 kV. The matrix employed was anthracene-1,8,9-triol–silver trifluoroacetate in THF. The MALDI-TOF gave a $[M+Ag]^+$ peak at 2046.4 which clearly confirms the structure of the cyclic tetramer.

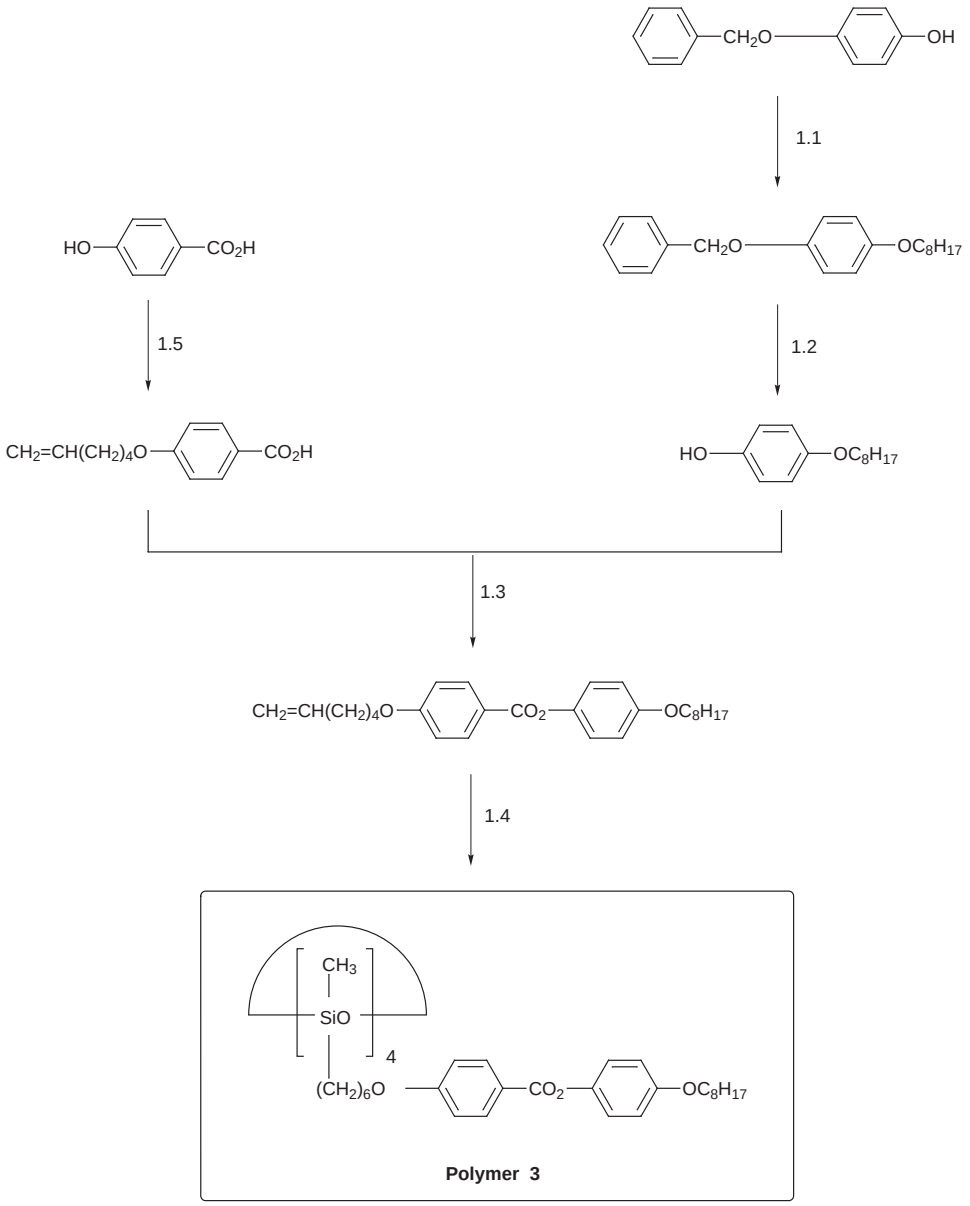
The SmA and SmC phases exhibited by the SCLC cyclic tetramer were confirmed by optical light microscopy and X-ray diffraction.

Preparation of Speiers catalyst

Hydrogen hexachloroplatinate(IV) (0.10 g) was dissolved in dry propan-2-ol (1 ml). Dry toluene (9 ml) was added with shaking and the solution was stored in the dark at 4 °C.

Preparation of 4-(hex-5-enyloxy)benzoic acid

The preparation of 4-(hex-5-enyloxy)benzoic acid was similar to that outlined in ref. 16. The cooled reaction mixture was acidified with concentrated hydrochloric acid (10 ml) and the crude product filtered off, washed with water and recrystallised (50% aqueous ethanol) to yield 4-(hex-5-enyloxy)benzoic acid as a white crystalline powder (purity, >99% by HPLC). Yield = 11.40 g (95%), transition temperatures K 101 N 140 °C Iso (lit.,[16] K 101 N 140 °C Iso). ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d), 6.95 (2H, d), 5.85 (1H, m), 5.05 (2H, t), 4.05 (2H, t), 2.15 (2H, m), 1.85 (2H, m), 1.60 (2H, m). IR (KBr) ν_{max} 2950, 1690, 1610, 1260 cm^{-1}. MS m/z 220 (M$^+$), 203, 138, 82, 55 (100%).



Scheme 1 *Reagents and conditions*: 1.1 1-Bromooctane, potassium carbonate, potassium iodide, butanone, 1.2 Cyclohexene, 5% palladium on charcoal, ethanol, glacial acetic acid; 1.3 DCC, DMAP, dichloromethane; 1.4 Pt catalyst, toluene; 1.5 6-Bromohex-1-ene, sodium hydroxide, water, ethanol.

Separation of the stereoisomers of the SCLC cyclic tetramer by HPLC

The following text details the use of HPLC in the separation of these stereoisomers.

Separation of stereoisomer 4

For the separation of stereoisomer 4 the following isocratic preparative HPLC system was used: Kontron HPLC pump 420, Gilson HPLC injection pump, Model 303, fitted with a 10-S pump head; Gilson automatic fraction collector 201 with 201–202 controller set for peak detection mode; Gilson Holochrome UV detector set at 254 nm; Dupont Instruments Zorbax ODS column (21.2 mm × 25 cm).

A standard solution of the SCLC cyclic tetramer was prepared by dissolving the tetramer (2.0 g) in chloroform (4 ml). Acetonitrile (6 ml) was then added dropwise to ensure that the polymer did not precipitate out of solution. A stock solution of chloroform–acetonitrile (40 : 60) was then prepared and used as the mobile phase. A metered volume of the standard solution (1.68 ml) was then injected onto the column, and the sample eluted at 5 ml min^{-1}. The fraction collector was programmed to identify individual peaks and set to collect individual fractions in sequence. Each sample peak was collected into a separate sample bottle.

The above procedure was repeated many times to yield sufficient sample to allow separation of the remaining isomers.

The HPLC chromatogram shown in Fig. 10 was obtained for the stereoisomer 4.

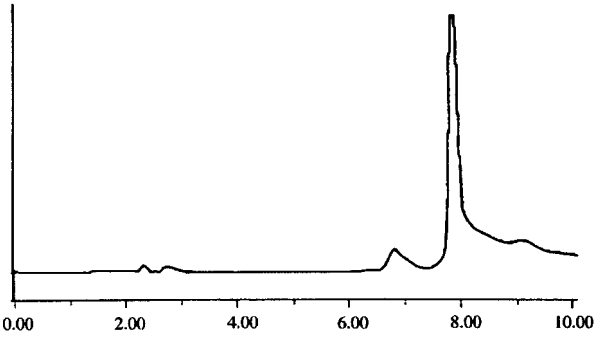


Fig. 10 The HPLC chromatogram of impure stereoisomer 4.

Purification of the stereoisomer 4

To ensure the complete separation of stereoisomer 4, it was necessary to further purify the above sample by using the following preparative gradient HPLC system: Merck/Hitachi L-6200A intelligent pump; Merck/Hitachi L-4000 UV detector, set at 254 nm; Merck/Hitachi D-6000 interface; Merck/Hitachi T-6300 column thermostat oven; Merck/Hitachi PC based data handling system; Dupont Zorbax ODS column (21.2 mm × 25 cm); Gilson Automatic fraction collector 201 with 201–202 controller set for manual peak collection mode.

The stereoisomer 4 (81.3 mg) from the previous separation was dissolved in chloroform (2 ml). Acetonitrile (3 ml) was then added slowly to ensure that the isomer did not precipitate out of solution. A known volume of sample (1 ml) was injected onto the column and the sample was eluted with the 50 : 50 chloroform–acetonitrile mixture for 2 min at a flow rate of 5 ml min^{-1}, at 30 °C. The mobile phase composition was then changed, using a gradient method, to chloroform–acetonitrile (35 : 65) over a period of 1 min. The process was then repeated a further 4 times until all the sample had been separated to yield pure stereoisomer 4. The solvent was then removed by distillation under reduced pressure and the isomer was then dried *in vacuo* to yield stereoisomer 4 as a white solid. Analytical HPLC showed that the purity of stereoisomer 4 was 100%.

The solvent in fractions containing stereoisomers 1, 2 and 3 was removed by distillation under reduced pressure, to yield a white solid which was used in the following section.

Separation of stereoisomers 1, 2 and 3

The preparative gradient HPLC system used in the purification of stereoisomer 4 was now used in the separation of stereoisomers 1, 2 and 3.

Separation of stereoisomer 3

A standard stock solution of the SCLC cyclic tetramer was prepared by dissolving the mixture of the three remaining isomers (0.01 g) in chloroform (2 ml). Acetonitrile (3 ml) was then added dropwise to ensure that the isomer did not precipitate out of solution.

Between injections, the sample solution and the syringe were stored in the column oven at 30 °C. This procedure was adopted to prevent the precipitation of isomers on standing. The column was then eluted with a mixture of chloroform–acetonitrile (40 : 60). A known volume of the sample solution (1 ml) was then injected onto the column, and the sample eluted at a flow rate of 4 ml min^{-1} at 30 °C. The sample peaks eluted from the column were collected manually and samples were collected allowing for a 'cut-off' sample between the major isomers. This method was used so that it was possible to isolate stereoisomer 3 in a pure state as well as concentrating the sample containing the remaining two isomers. The above procedure was repeated many times to yield sufficient sample of stereoisomer 3.

The solvent was then removed, under reduced pressure, and the residue dried *in vacuo* to yield stereoisomer 3 as a white solid. Analytical HPLC showed that the purity of stereoisomer 3 was 100%.

The solvent in fractions containing stereoisomers 1 and 2 was distilled off, under reduced pressure, to yield a white solid which was used in the separation of stereoisomers 1 and 2.

Separation of the remaining two stereoisomers 1 and 2

The method used for the separation of the remaining two isomers was identical to that outlined previously. The sample was prepared in a similar manner to that outlined for the separation of stereoisomer 3, but the injection volume was reduced to 0.5 ml. The eluent system that was used in the separation of the remaining two isomers was a mixture of chloroform–acetonitrile (30 : 70), with a column oven temperature of 30 °C.

Again the multiple injection method was used in conjunction with our 'cut-off' method to achieve the separation of the two remaining stereoisomers in a pure state.

The fractions containing pure stereoisomer 1 were combined and the solvent removed by distillation under reduced pressure to afford pure stereoisomer 1 as a white solid (100% pure by analytical HPLC). This procedure was also carried out to obtain a pure sample of stereoisomer 2 (white solid, 100% pure by analytical HPLC).

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