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Synthesis and characterization of some new dimesogenic compounds

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We have synthesized four different types of dimesogenic compounds involving the cholesteryl moiety as one of the mesogenic constituents, and have investigated their liquid crystalline properties. The molecular structures of these dimesogens have been confirmed by spectral analyses; they exhibit a rich polymorphism, as revealed by optical microscopic and differential scanning calorimetric observations. The studies show that the mesomorphic behaviour is sensitive to the nature of the terminal alkyl chains, and to the structure of the 'second mesogen' that is attached to the cholesteryl unit through a polymethylene spacer.

1. Introduction

Currently liquid crystalline dimers (also known as twins or dimesogens) are attracting attention owing to the variety of phases they exhibit [1]. In typical dimesogens, two individual mesogenic entities are attached to each other via flexible polymethylene spacer units. Symmetrical dimesogens in which the two mesogenic units are identical are well studied systems [2], partly because of the ease of their synthesis. In contrast, studies on non-symmetrical compounds remain unexplored, although a few systems [3*a*, *b*], including chiral ones [3*c*], are known. In this paper we restrict ourselves to non-symmetrical dimesogens involving the cholesteryl moiety as one of the constituents. Recently, the synthesis and characterization of a similar cholesteryl-based dimesogenic compound has been reported [4]. This compound, which we refer to as KI-5, is made up of a cholesteryl moiety and a Schiff's base mesogen joined by a flexible paraffinic spacer unit, and exhibits an interesting polymorphic sequence including incommensurate smectic phases. Further studies on similar type of compounds [5] showed that the length of the spacer is crucial for the occurrence of the incommensurate phase as compared with the appearance of other mesophases, viz. the blue phase, the twist grain boundary (TGB) phase and the smectic C phase, which are not so sensitive to the length of the spacer. It was also noticed that the type of bridging group between the two aromatic rings of the non-cholesteryl moiety affects the stability of the different mesophases [6].

As possible variations on the structure of KI-5, we have introduced a long alkyl chain, and different types of chiral moieties on the Schiff's base unit; this will assist in the study and understanding of the structure–property relationship in these dimesogens. Here we report the synthesis and characterization of four new dimesogens having a long alkyl chain, a chiral ester chain or a chiral 1,3-dioxalane ring at the 4-position of the Schiff's base benzene ring moiety. The molecular structures of these compounds are shown in figure 1. For comparison we also show the structure of KI-5.

2. Results and discussion

2.1. *Synthesis*

These new dimesogens (DMS-1 to 4) were synthesized starting from aldehyde **8**. This key intermediate was obtained by reacting 4-hydroxybenzaldehyde with cholesteryl 6-bromohexanoate (**7**) in the presence of anhydrous potassium carbonate in acetone under reflux. 4-(*n*-Dodecyl)aniline (**6**) was synthesized by the reaction of 4-nitrobenzaldehyde with *n*-undecylidenetriphenylphosphorane in dry THF, followed by catalytic hydrogenation of the resulting nitrostyrene derivative **5**. The dimesogen DMS-1 was then obtained by the condensation reaction between amine **6** and aldehyde **8** (see scheme 1). The dimesogens DMS-2 and DMS-3 were synthesized as outlined in scheme 2. Initially

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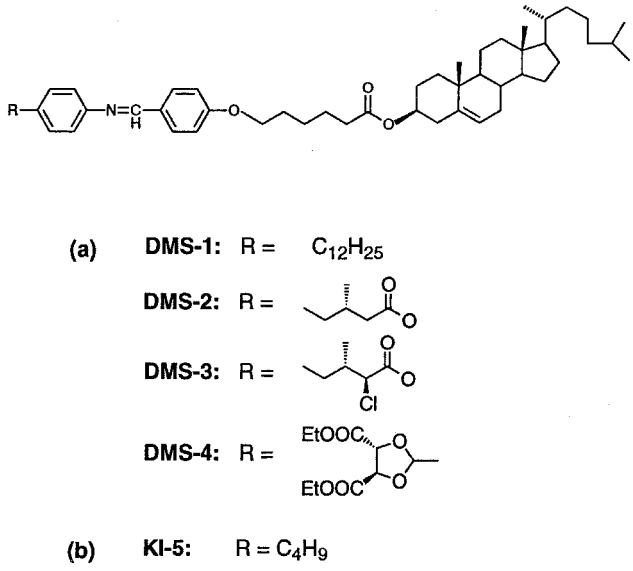


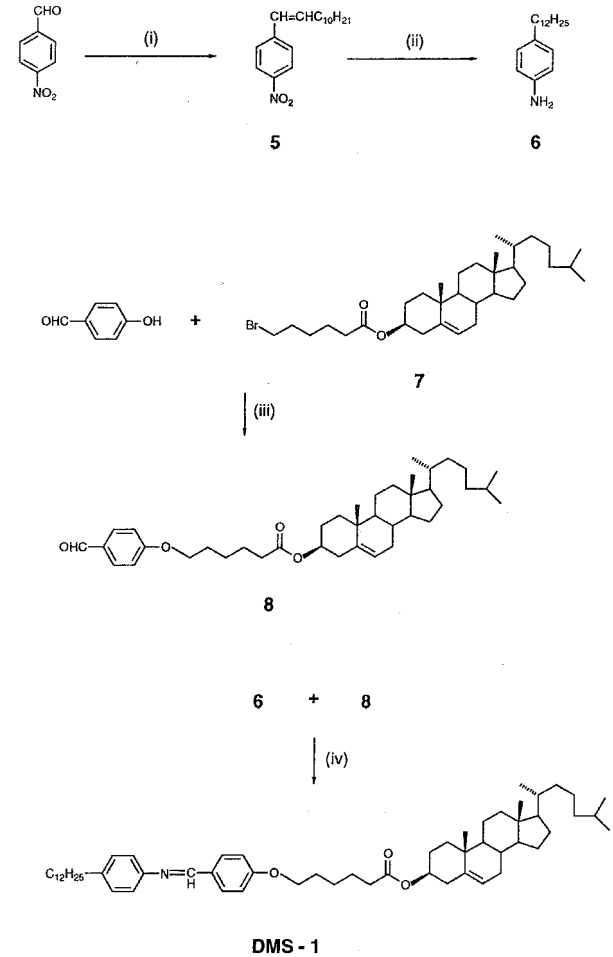
Figure 1. (*a*) Molecular structure of the dimesogens DMS-1, 2, 3, 4; (*b*) structure of dimesogen KI-5.

4-nitrophenol was esterified with 2*S*-chloro-3*S*-methylpentanoyl chloride (**9**) in the presence of pyridine to provide nitroester **10**. The amine **11** was obtained by catalytic hydrogenation of nitroester **10**, wherein reduction of the nitro functional group and dechlorination occur simultaneously. The amine **11** was heated under reflux in benzene with aldehyde **8** to give DMS-2. Controlled catalytic hydrogenation of the nitroester **10** furnished the amine **12**, which upon treatment with aldehyde **8** gave DMS-3. DMS-4 was synthesized following the synthetic sequence described in scheme 3. The nitroacetal **13** was obtained by acetalization of 4-nitrobenzaldehyde with optically active (+)-L-diethyl tartarate; controlled catalytic hydrogenation of **13** afforded the amine **14**. Condensation of the amine **14** with the aldehyde **8** furnished DMS-4. Details of all syntheses are given in §3.

2.2. *Thermal behaviour*

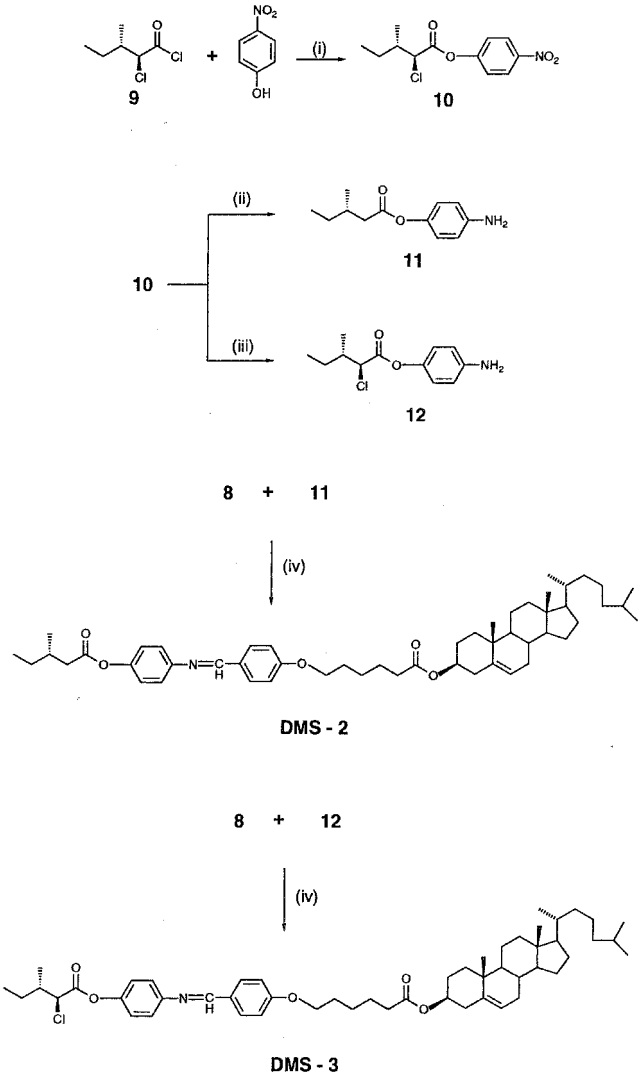
As regards the existence of the incommensurate phase with modifications to the structure KI-5, the following points have been observed [5, 6*a*]: (*i*) altering the central alkyl spacer from C_5 to C_4, C_7 or C_{10} results in the absence of the incommensurate phase despite the presence of the blue phases, the cholesteric, TGB and SmA phases [5]; (*ii*) changing the linking group from an imine to an azo group (N=N), also leads to the disappearance of the incommensurate phase [6*a*]; (*iii*) modifying the terminal chain of the Schiff's base unit from C_4H_9 to $CH{=}CHCOOC_2H_5$ stabilizes the incommensurate phase [6*b*].

Structurally, DMS-1 represents the simplest change made to KI-5, namely, an increase in the terminal alkyl chain length substitution from C_4 to C_{12} (see figure 1).

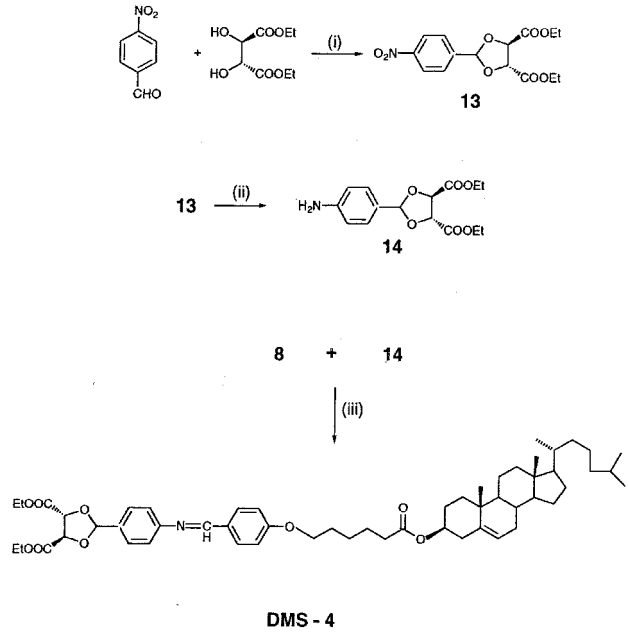


Scheme 1. Synthetic route to DMS-1. (i) $BrPh_3P^+CH_2C_{10}H_{21}$ / *n*-BuLi, dry THF, rt, 15 h. (ii) Pd-C (10%)/H_2, EtOH, 40 psi, 2 h. (iii) K_2CO_3 /dry acetone, reflux, 20 h. (iv) C_6H_6, reflux, 4 h.

KI-5, with C_4 normal alkyl chain substitution shows a rich variety of phases, e.g. blue phase, cholesteric, TGB phase and smectic C* (SmC*) phases in addition to the smectic incommensurate phase. But in contrast DMS-1, with a longer alkyl chain length, shows only two mesophases. Optical microscopic observations show that the phase immediately below the isotropic (I) phase is a smectic A (SmA) phase, exhibiting the characteristic focal-conic texture in slides treated for planar orientation, and a dark field of view in slides treated for homeotropic orientation. Below 105°C the slides treated for homeotropic alignment show a texture with a milky white appearance. In planar oriented samples no pitch lines were seen on top of the focal-conic fan texture; this suggests that the low temperature mesophase is a SmC* phase with a pitch value which lies outside the visible wavelength range (see, e.g. [7]). DSC traces (figure 2) taken for DMS-1 show only one peak corresponding



Scheme 2. Synthetic route to DMS-2 and DMS-3. (i) Dry pyridine/THF, 20 h. (ii) Pd-C (10%)/H_2, EtOH, 40 psi, 4 h. (iii) Pd-C (5%)/H_2, EtOH, 1 atm, 3 h. (iv) C_6H_6, reflux, 4 h.



Scheme 3. Synthetic route to DMS-4. (i) PTSA/C_6H_6, reflux, 24 h. (ii) Pd-C (5%)/H_2, 15 psi, 45 min. (iii) C_6H_6, reflux, 4 h.

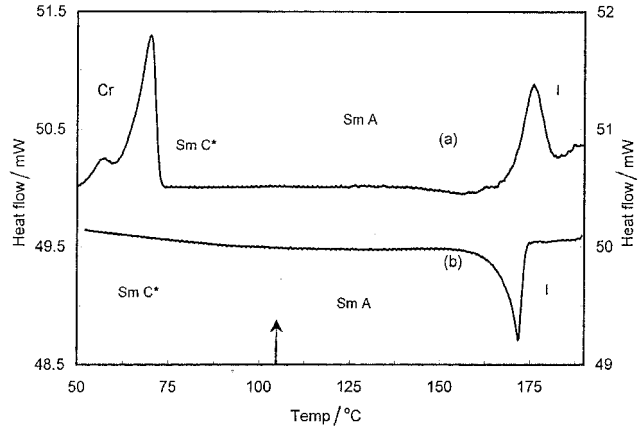


Figure 2. DSC thermograms for DMS-1 in the (*a*) heating and (*b*) cooling modes. In this figure and also in figures 4 and 8 the scale for the heating curve is indicated on the left and for the cooling scan on the right. The arrow indicates the temperature at which the SmA–SmC* transition is observed in optical microscopy.

to the I–SmA transition but no signature for the SmA–SmC* transition. The latter feature is not surprising as it is well known that in materials having a large temperature range for the SmA phase the SmA–SmC transition is second order [8]. The X-ray diffraction pattern obtained using a Guinier diffractometer at a temperature of about 140°C was quite similar to that observed in the incommensurate smectic phase of KI-5. More specifically, three sharp reflections whose wave vectors are in the ratio of 1:1.9:2.1 were seen. These values, as well as the intensity ratios, compared very well (1:1.8:2.2) with those obtained for KI-5 [4*b*]. Thus, one is strongly tempted to conclude that the high temperature smectic phase in DMS-1 is an incommensurate one. However, as the diffractometer set-up permits only a one-dimensional scan this result needs to be confirmed by taking pictures in two-dimensional reciprocal space.

With a view to studying the influence of introducing chirality on the Schiff's base moiety side also, we synthesized three different types of mesogens. DMS-2 shows the simplest of such substitutions. Here the 'core' of the Schiff's base part was terminated with an ester linkage having a chiral methyl substitution at the β-position of the carbonyl functional group. Thus, DMS-2 differs from

KI-5 only in the ester linkage and the asymmetric carbon atom substitution. With this in mind we investigated the thermal behaviour of DMS-2 using DSC as well as optical microscopy. On cooling the isotropic phase, a cholesteric phase with the characteristic fingerprint texture was seen. On further cooling, a TGB phase appeared over a very short temperature interval of about ~0.5°C before transforming into a SmA phase. The TGB phase showed the usual filament type texture (figure 3). No further phase transitions were observed before crystallization. The DSC scan (figure 4) showed a strong peak with a large enthalpy value for the isotropic–cholesteric (Ch) transition. A single peak was observed in the temperature region corresponding to the Ch–TGB and TGB–SmA transitions with a very low heat of transition (see the table). We were unable to resolve peaks of the two transitions because the range of the TGB phase was very small.

Comparing these features with those reported for KI-5, one can note that (*i*) even a small modification to the structure of KI-5 alters the phase sequences significantly, (*ii*) despite the larger polarizability of the DMS-2

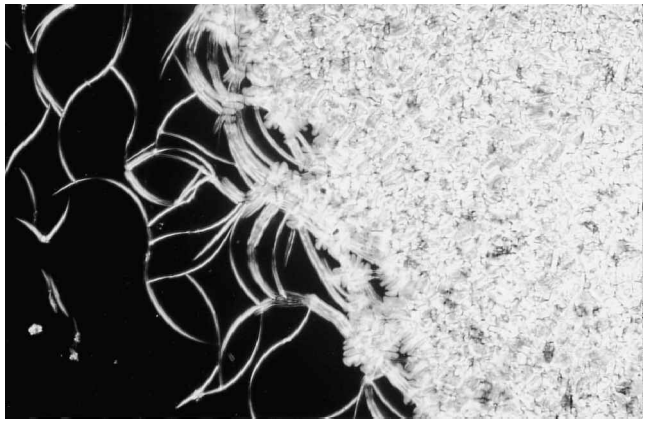


Figure 3. Characteristic filament texture (middle portion of the photograph) exhibited by the TGB phase of DMS-2, as seen growing from the homeotropic SmA phase (dark region on the left). As the range of the TGB phase is only 0.5°C and both the SmA–TGB and TGB–Ch transitions are broad, one can see the texture corresponding to the cholesteric phase on the right hand side of the photograph (temperature = 169.5°C, × 160 magnification).

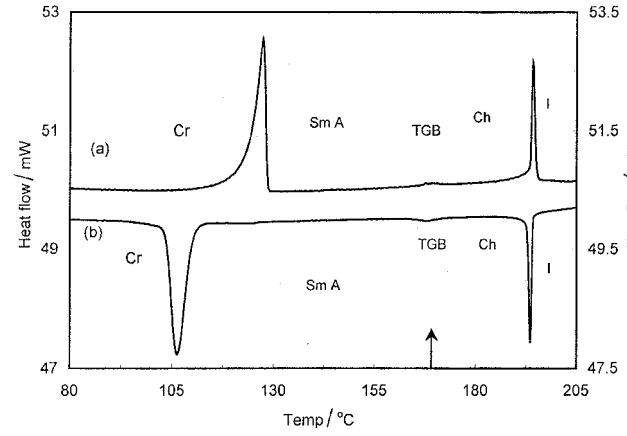


Figure 4. DSC thermograms for DMS-2. Only one weak peak was observed, in the temperature region that is indicated by the arrow, and corresponding to the Ch–TGB, TGB–SmA transitions.

Table. Transition temperatures[a] (in °C) and enthalpies (J g^{-1}) of the dimesogens reported. The enthalpy values are enclosed in square brackets. Cr = crystal; SmC* = chiral smectic C phase; SmA = smectic A phase; SmA_{inc} = incommensurate smectic A phase; TGB = twist grain boundary phase; Ch = cholesteric; I = isotropic liquid; ( ) = monotropic phase.

DMS-1	$Cr \xrightarrow[[28.54]]{63.6} SmC^* \xrightarrow[[\sim 0]]{104.8} SmA \xrightarrow[[13.21]]{174.7} I$
DMS-2	$Cr \xrightarrow[[20.54]]{127.65} SmA \xrightarrow{169.1} \underset{[0.561]}{TGB_b} \xrightarrow{169.5} Ch \xrightarrow[[3.92]]{193.2} I$
DMS-3	$Cr \xrightarrow[[20.74]]{120.7} Sm1^c \xrightarrow[[1.21]]{150.5} Sm2^c \xrightarrow{165.6} \underset{[0.36]}{TGB_b} \xrightarrow{165.7} Ch \xrightarrow[[4.6]]{185.4} I$
DMS-4	$Cr \xrightarrow[[19.18]]{105.35} SmA \xrightarrow[[0.14]]{123.5} Ch \xrightarrow[[3.08]]{148.5} I$ $SmC^* \xleftarrow[[\sim 0]]{(84.2)}$
KI-5[4]	$K \xrightarrow{85} SmA_{inc} \xrightarrow{144.5} SmC^* \xrightarrow{149} SmA_{inc} \xrightarrow{151.5} SmC^* \xrightarrow{165} TGB \xrightarrow{168} Ch \xrightarrow{192} I$

[a] Peak temperature in the DSC thermograms were taken as transition temperatures.

[b] Although SmA–TGB (Sm2–TGB in DMS-3), TGB–Ch transition was observed under the microscope, this transition was not resolved in the DSC scan. Hence the ΔH value in both DMS-2 and DMS-3 represents the combined enthalpy for both SmA–TGB (Sm2–TGB in DMS-3) and TGB–Ch transitions.

[c] Sm1 and Sm2 are seen to be smectic phases but their precise structure is yet to be confirmed.

molecule (owing to the presence of the ester group), the clearing point temperature seems to be hardly affected.

In the compound DMS-3, the chirality of the Schiff's base part was further increased by incorporating an additional chiral centre with a strongly polar chlorine atom attached at the α-position of the carbonyl functional group. Optical observations showed a similar phase sequence to that seen for DMS-2, except that the TGB phase appeared only as a transient phase (temperature range < 0.1°C). This observation is slightly puzzling because the available data in the literature indicate that the TGB phase is stabilized in compounds which are highly chiral [9]. As seen in the DSC scan (figure 5) there is a significantly strong peak around 150°C. Optical observations showed in the high temperature mesophase (i.e. above 150°C) the existence of bands superposed over the back of focal-conics (figure 6). On cooling below 150°C these bands disappear and the edges of focal-conics become sharper (figure 7). In homeotropically aligned samples the field of view remained dark through this transition. The absence of any electrical switching in both the phases precludes the possibility of the occurrence of a chiral mesophase. As the compound was thermally unstable we were unable to carry out X-ray studies on these phases.

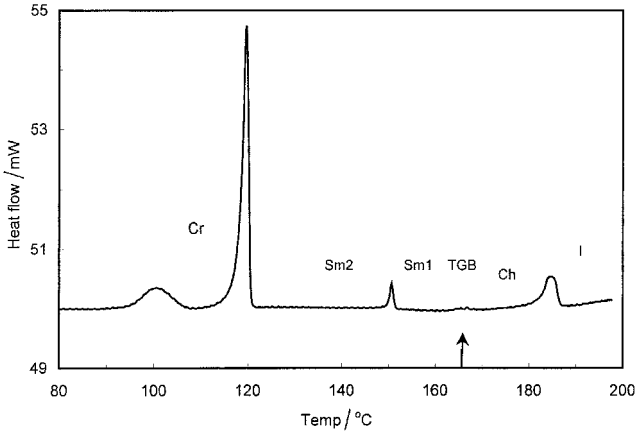


Figure 5. DSC thermograms for DMS-3 in the heating mode. Note the strong peak at around 150°C. The nature of the mesophases above and below 150°C is yet to be identified; the high temperature phase is denoted Sm1, the low temperature phase Sm2. Since the compound was thermally unstable only the heating mode scan is given.

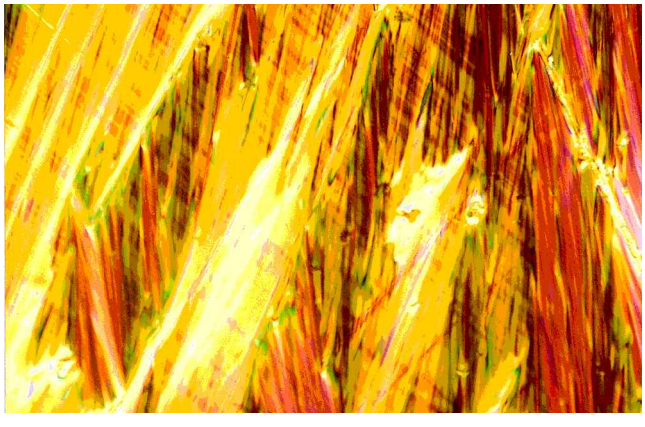


Figure 6. Texture photograph of DMS-3 at a temperature of 155°C (Sm1 phase). Note the bands superposed over the back of focal conics (× 160 magnification).

Another modification to the structure of KI-5 that we have examined is represented in the dimesogen DMS-4. Here we introduced two features, viz. cyclic (1,3-dioxalane) termination of the core and two vicinal chiral centres having the same functionality attached in a 'swallow-tail' manner at the 1,3-dioxalane ring. A dramatic effect that we observe is the change in the clearing temperature. Compared with KI-5, the I–Ch transition decreases by about 50°C. This may be explained by the presence of the 'swallow-tail' structure. A lowering is also observed for the Ch–SmA and SmA–SmC* transition temperatures (see table; for DSC traces see figure 8). No pitch lines were seen in the smectic C* phase for planar orientation, but in the homeotropic samples a milky white texture was observed indicating that the helical pitch value lies outside the visible range.

The phase transition temperatures of all the four dimesogens are summarized in the table.

3. Experimental

Chemicals and solvents (Ar quality) were obtained from Fluka or Aldrich or a local source, and used as such without purification. Column chromatographic separations were performed using either silica gel (230–400 mesh) or neutral aluminium oxide. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel0, F254). IR spectra

Figure 7. Texture photograph of DMS-3 at 115°C (Sm2 phase). Comparing with figure 6 it can be seen that the bands disappear and focal-conics are sharpened (× 160 magnification).

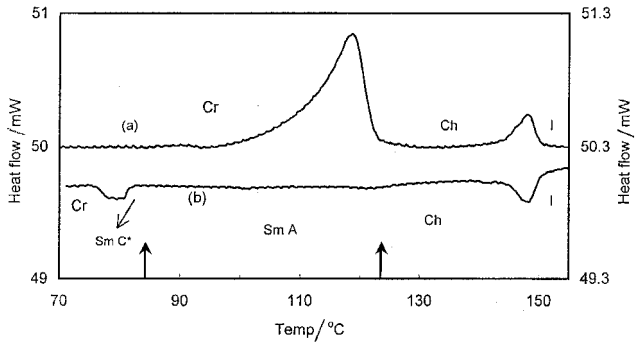


Figure 8. DSC scan for DMS-4. Note the appreciable decrease in the I–Ch, Ch–SmA transition temperatures when compared with those for the other dimesogens reported here.

were recorded using a Shimadzu IR-435 or Perkin Elmer 781 spectrophotometer. ^{1}H NMR spectra were recorded using Bruker DRX400 (400 MHz), Bruker ACF-200 (200 MHz), Bruker WH-270 (270 MHz), Jeol-90Q (90 MHz) or Jeol JNMλ 300 (300 MHz) spectrometers using $CDCl_3$ as solvent. For ^{1}H NMR spectra, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard; coupling constant (J) values are given in Hz. Mass spectra were recorded on a Finnigan mat 90 spectrometer.

The compounds were investigated for liquid crystalline behaviour with the help of an optical polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90) and by differential scanning calorimetry (Perkin Elmer DSC7). Optical observations were made with two different surface-coated slides, one treated for homogeneous alignment and another for homeotropic alignment. The rate of heating and cooling for DSC was 5°C min^{-1}, for optical microscopic studies it was 1°C min^{-1}.

3.1. *4-n-Dodecylaniline (**6**)*

This compound was synthesized via the nitro olefinic compound **5** which in turn was prepared as follows. To a magnetically stirred solution of undecylphosphonium salt (1.5 g, 3 mmol) in dry THF (10 ml) *n*-BuLi (2 ml, 3.3 mmol) was added slowly over a period of 5 min at 0°C under nitrogen. The orange coloured suspension was stirred for 5 min at 0°C and then was added a solution *p*-nitrobenzaldehyde (0.45 g, 3 mmol) in THF (10 ml) over a period of 10 min. The dark brown suspension was stirred at r.t. for 15 h. Excess THF was removed *in vacuo* and the dark brown semi-solid was poured into ice-cold water. The mixture was extracted with ether (3 × 10 ml), washed with water and the combined organic layer was filtered through a celite bed and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the resulting dark brown oil purified by column chromatography over silica gel. Elution with 10% EtOAc–hexane yielded a pale yellow oil, 0.53 g (66%) of compound **5**. IR (Neat): 2910, 2820 and 1590 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): 8.16 (m, 2H, Ar), 7.41 (m, 2H, Ar), 6.44 (m, 1H, olefinic), 5.85 (m, 1H, olefinic), 2.31 (t, 2H, J = 6.3, C=C–CH_2), 1.38 (brm, 16H, 8 × CH_2) and 0.86 (t, 3H, J = 9, CH_3).

A mixture of compound **5** (0.53 g, 1.83 mmol), absolute ethanol (15 ml) and Pd-C (10%) (10 mg) was hydrogenated at 40 psi pressure over a period of 2 h. The reaction mixture was filtered through a celite bed and the solvent was evaporated *in vacuo* to give a dark yellow oil. This was purified by column chromatography over silica gel. Elution with 15% EtOAc–hexane yielded compound **6** as a pale yellow oil, 0.45 g (94%). IR (Neat): 3360, 2900, 2840 and 1620 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): 6.95 (brd, J = 7, 2H, Ar), 6.58 (d, 2H, J = 11.7, Ar), 3.41 (brs, 2H, –NH_2), 2.49 (t, 2H, J = 5.4, Ar–CH_2), 1.3 (brs, 20H, 10 × CH_2) and 0.85 (brt, 3H, J = 4.5, CH_3).

3.2. *Cholesteryl 6-(4-formylphenoxy)hexanoate (**8**)*

A mixture of cholesteryl 6-bromohexanoate (**7**) (1.5 g, 2.66 mmol), 4-hydroxybenzaldehyde (0.34 g, 2.79 mmol) and anhydrous potassium carbonate (7 g, 50.6 mmol) in acetone (25 ml) was heated at reflux for 20 h. The hot reaction mixture was filtered through a celite bed and the filtrate was concentrated *in vacuo* to give a off-white solid. The solid was dissolved in ether (30 ml), and the solution washed with 0.01 N sodium hydroxide solution (10 × 3 ml), water and then with brine. The solution was dried over sodium sulphate and the solvent evaporated to yield an almost white solid which was purified by column chromatography over neutral alumina. Elution with 10% EtOAc–hexane furnished white solid compound **8**, 1.2 g (75%), m.p. 123–124°C. IR (Nujol): 1722 and 1689 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 9.8 (s, 1H, –CHO), 7.83 (d, J = 9, 2H, Ar), 6.98 (d, J = 8.7, 2H, Ar), 5.37 (brd, J = 4.8, 1H, olefinic), 4.6 (brm, 1H, CHOH), 4.04 (t, J = 6.3, 2H, 1 × OCH_2), 2.32 (m, 4H, 2 × C=CH_2), 2.1–0.98 (m, 32H, 13 × CH_2, 6 × CH), 1.01 (s, 3H, CH_3), 0.91 (d, J = 6.9, 3H, CH_3), 0.87 (d, J = 1.2, 3H, CH_3), 0.85 (d, J = 1.2, 3H, CH_3) and 0.68 (s, 3H, CH_3).

3.3. *Cholesteryl 6-[4-(4-n-dodecylphenyliminomethyl)-phenoxy]hexanoate: DMS-1*

A mixture of aldehyde **8** (0.35 g, 0.58 mmol) and 4-*n*-dodecylaniline (**6**) (0.151 g, 0.58 mmol) in dry benzene (15 ml) was placed in a Dean–Stark apparatus and heated under reflux for 4 h under anhydrous condition. The reaction mixture was concentrated to give a pale yellow semi-solid which was purified by repeated

recrystallization (5 times) from *n*-butanol to yield white solid compound DMS-1, 0.3 g (61%). IR (KBr): 3430, 2900, 2850, 1710 and 1605 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): 8.39 (s, 1H, –CH=N), 7.82 (d, 2H, J = 8.6, Ar), 7.15 (ABq, 4H, Ar), 6.95 (d, J = 8.6, 2H, Ar), 5.37 (brd, J = 4.6, 1H, olefinic), 4.62 (brm, 1H, CHOH), 4.02 (t, J = 6.3, 2H, $-OCH_2$), 2.62 (t, J = 7.2, 2H, Ar–CH_2), 2.32 (m, 4H, 2 × C=CH_2), 2.03–0.85 (m, 55H, 1 × CH_3, 23 × CH_2, 6 × CH), 1.01 (s, 3H, CH_3), 0.97 (d, J = 5.8, 3H, CH_3), 0.91 (d, J = 1.5, 3H, CH_3), 0.86 (d, J = 1.38, 3H, CH_3), and 0.68 (s, 3H, CH_3).

3.4. *4-(2S-Chloro-3S-methylpentanoyloxy)nitrobenzene (**10**)*

To magnetically stirred 2*S*-chloro-3*S*-methylpentanoyl chloride (**9**) (1.12 g, 6.62 mmol) was added a solution of 4-nitrophenol (0.92 g, 6.62 mmol) and pyridine (1 ml) in dry THF (15 ml) over a period of 15 min at 0–5°C under nitrogen. The reaction mixture was allowed to warm to room temperature and then stirred for 20 h. It was concentrated and then diluted with ether (30 ml). The ether layer was washed with aq 0.01N HCl (20 ml), aq 0.01N NaOH (20 ml) and water, and then dried over anhydrous sodium sulphate. Evaporation of the solvent furnished a dark yellow thick liquid which was purified by column chromatography over neutral alumina. Elution with dichloromethane yielded compound **10** as a pale yellow oil, 0.92 g (51%). IR (Neat): 3050, 2970, 1770 and 1610 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): 8.31 (d, 2H, J = 9, Ar), 7.36 (d, J = 10, 2H, Ar), 4.38 (d, J = 7.2, 1H, CHCl), 2.18 (m, 1H, CH), 1.51 (m, 2H, CH_2), 1.16 (d, J = 8.1, 3H, CH_3) and 0.93 (t, J = 3.6, 3H, CH_3).

3.5. *4-(3S-Methylpentanoyloxy)aniline (**11**)*

A mixture of 4-(2*S*-chloro-3*S*-methylpentanoyloxy)-nitrobenzene (**10**) (0.92 g, 3.38 mmol), Pd-C (10%) (150 mg) and absolute ethanol (30 ml) was hydrogenated at 40 psi pressure for 4 h. The reaction mixture was filtered through a celite bed and the filtrate was concentrated *in vacuo*. The crude dark brown solid obtained was washed with hexanes several times to give compound **11** as a pale brown solid which was pure enough to use in the next step (this amine seemed to be unstable and therefore was used immediately). Yield: 0.63 g (90%). IR (Nujol): 3340, 3305, 3200, 1710 and 1640 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): 6.86 (m, 2H, Ar), 6.61 (d, 2H, J = 8.1, Ar), 3.06 (s, 2H, $-NH_2$), 2.39–1.01 (m, 5H, 2 × CH_2 and CH), 1.09 (d, J = 8.7, 3H, CH_3), and 0.92 (t, J = 3.8, 3H, CH_3).

3.6. *Cholesteryl 6-[4-(3S-methylpentanoyloxyphenyl-iminomethyl)phenoxy]hexanoate: DMS-2*

DMS-2 was prepared following a similar procedure to that described for DMS-1. Yield of white solid: 0.37 g (81%). IR (KBr pellet): 3410, 2907, 1755, 1720, 1610 and 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz); 8.3 (s, 1H, –CH=N), 7.75 (d, J = 8.72, 2H, Ar), 7.13 (d, J = 1.84, 2H, Ar), 7.02 (d, J = 2.64, 2H, Ar), 6.92 (d, J = 9.28, 2H, Ar), 5.30 (brd, J = 3.92, 1H, olefinic), 4.56 (m, 1H, CHOH), 3.97 (t, J = 4, 2H, $-OCH_2$), 2.52–0.97 (m, 44H, 17 × CH_2, 7 × CH, 1 × CH_3), 0.99 (d, J = 6.64, 3H, CH_3), 0.95 (s, 3H, CH_3), 0.85 (d, J = 6.48, 3H, CH_3), 0.81 (d, J = 1.48, 3H, CH_3), 0.79 (d, J = 1.48, 3H, CH_3), and 0.61 (s, 3H, CH_3); FAB MS *m/z*: 794 {$[MH]^+$; $C_{52}H_{75}NO_5$}, 695 {$[MH]^+ - C_6H_{11}O(99)$}$^+$, 426 {$[MH]^+ - C_{27}H_{44}(368)$}$^+$ and 327 $[426-C_6H_{11}O(99)]^+$.

3.7. *4-(2S-Chloro-3S-methylpentanoyloxy)aniline (**12**)*

A mixture of 4-(2*S*-chloro-3*S*-methylpentanoyloxy)-nitrobenzene (**10**) (0.92 g, 3.38 mmol), Pd-C (5%) (50 mg) and absolute ethanol (30 ml) was hydrogenated at 15 psi pressure for 3 h (TLC monitored). Working up as described for **11** yielded pale brown solid compound **12**, 0.67 g (83%). IR (Nujol): 3456, 3300, 3202, 1755 and 1620 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz), 6.88 (m, 2H, Ar), 6.61 (d, J = 8.9, 2H, Ar), 4.3 (d, J = 9, 1H, CHCl), 3.04 (s, 2H, $-NH_2$), 2.42–1.0 (m, 3H, 1 × CH_2, 1 × CH), 1.06 (d, J = 8.7, 3H, CH_3) and 0.90 (t, J = 3.8, 3H, CH_3).

3.8. *Cholesteryl 6-[4-(2S-chloro-3S-methylpentanoyloxy-phenyliminomethyl)phenoxy]hexanoate: DMS-3*

DMS-3 was prepared following a similar procedure to that described for DMS-1. Yield of white solid: 0.34 g (71%). IR (KBr pellet): 3490, 3050, 2990, 1780, 1720 and 1610 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz); 8.36 (s, 1H, –CH=N–), 7.82 (d, J = 7.4, 2H, Ar), 7.22 (m, 2H, Ar), 7.13 (m, 2H, Ar), 6.96 (d, J = 7.32, 2H, Ar), 5.37 (brd, J = 4.84, 1H, olefinic), 4.65 (brm, 1H, CHOH), 4.38 (d, J = 7.08, 1H, CHCl), 4.05 (t, J = 6.32, 2H, OCH_2), 2.56–0.99 (m, 39H, 16 × CH_2, 7 × CH), 0.98 (d, J = 5.08, 3H, CH_3), 0.95 (s, 3H, CH_3) 0.92 (t, J = 6.12, 3H, CH_3), 0.87 (d, J = 6.3, 3H, CH_3), 0.8 (d, J = 1.76, 3H, CH_3), 0.79 (d, J = 1.76, 3H, CH_3) and 0.60 (s, 3H, CH_3).

3.9. *4-[4R,5R-Bis(ethoxycarbonyl)-1,3-dioxalan-2-yl]-nitrobenzene (**13**)*

A mixture of *p*-nitrobenzaldehyde (1 g, 6.62 mmol), (+)-L-diethyltartrate (1.36 g, 6.62 mmol) and *p*-toluene-sulphonic acid (50 mg) in dry benzene (50 ml) was heated under reflux in a Dean–Stark apparatus for 24 h. The reaction mixture was cooled to room temperature and poured into ice-cold 10% aq. $NaHCO_3$ solution (30 ml). It was then extracted with dichloromethane (stored over basic alumina) (3 × 25 ml). The combined organic layers were washed with water, then brine, and passed through anhydrous potassium carbonate. Evaporation of the solvent yielded a pale yellow solid which was recrystallized from hexanes to give colourless solid compound **13**

(this was used in the next step immediately). Yield: 1.3 g (59%). IR (Nujol): 1735 and 1615 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz); 8.26 (d, $J = 8.7$, 2H, Ar), 7.79 (d, $J = 8.67$, 2H, Ar), 6.26 (s, 1H, CH–Ar), 4.97 (d, $J = 3.66$, 1H, CH), 4.87 (d, $J = 3.63$, 1H, CH), 4.31 (m, 4H, $2 \times CH_2$) and 1.37 (m, 6H, $2 \times CH_3$).

3.10. *4-[4R,5R-Bis(ethoxycarbonyl)-1,3-dioxalan-2-yl]-aniline (**14**)*

A mixture of compound **13** (1.1 g, 3.24 mmol), Pd-C (5%) (80 mg) and absolute ethanol (20 ml) was hydrogenated at 15 psi pressure for 45 min (TLC monitored). The reaction mixture was filtered through celite and the filtrate concentrated *in vacuo*; the compound **14** product was used immediately without purification. Yield: 0.91 g (quantitative). IR (Nujol): 3460, 3365, 2960, 1730 and 1610 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz), 7.35 (d, $J = 9.9$, 2H, Ar), 6.65 (d, $J = 10.1$, 2H, Ar), 6.05 (s, 1H, CH–Ar), 4.92 (d, $J = 4.5$, 1H, CH), 4.78 (d, $J = 5.1$, 1H, CH), 4.32 (m, 4H, $2 \times CH_2$), 3.24 (brs, 2H, $-NH_2$) and 1.34 (m, 6H, $2 \times CH_3$).

3.11. *Cholesteryl 6-{4-[[4R,5R-bis(ethoxycarbonyl)-1,3-dioxalan-2-yl]phenyliminomethyl]phenoxy}-hexanoate: DMS-4*

DMS-4 was prepared following a similar procedure to that prescribed for DMS-1. Yield of pale yellow solid: 0.18 g (35%). IR (KBr pellet): 3480, 2980, 1730, 1717 and 1605 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): 8.35 (s, 1H, CH=N), 7.83 (d, $J = 8.64$, 2H, Ar), 7.60 (d, $J = 8.32$, 2H, Ar), 7.20 (d, $J = 8.37$, 2H, Ar), 6.96 (d, $J = 8.64$, 2H, Ar), 6.17 (s, 1H, CH–Ar), 5.38 (brd, $J = 4.04$, 1H, olefinic), 4.96 (d, $J = 3.94$, 1H, CH), 4.84 (d, $J = 4$, 1H, CH) 4.64 (m, 1H, CHOH), 4.33 (m, 4H, $2 \times CH_2$), 4.03 (t, $J = 6.3$, 2H, OCH_2), 2.35–0.98 (m, 36H, $15 \times CH_2$, $6 \times CH$), 1.36 (m, 6H, $2 \times CH_3$), 1.02 (s, 3H, CH_3), 0.97 (d, $J = 3.8$, 3H, CH_3), 0.91 (d, $J = 6.42$, 3H, CH_3), 0.86 (d, $J = 6.56$, 3H, CH_3) and 0.68 (s, 3H, CH_3).

4. Conclusions

We have synthesized four different modifications of KI-5, a non-symmetrical cholesterol based dimesogen, first reported by Jin *et al.* [4]. Our main findings are: (1) increase in the alkyl chain length decreases the number of mesophases observed; (2) a chiral end chain does not stabilize the TGB phase, a result which appears to be contra-intutive; (3) a cyclic termination of the core with two vicinal chiral centres leads to a drastic reduction in the clearing temperature. Investigations on other modifications are in progress.

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