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Cholesterol-based dimeric liquid crystals: synthesis and mesomorphic behaviour

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Chiral non-symmetric dimeric liquid crystals consisting of a cholesteryl ester moiety as chiral entity and a biphenyl aromatic core, interconnected through *n*-butyl (C_4) or *n*-pentyl (C_5) parity alkylene spacers, have been synthesized and investigated for their liquid crystalline properties. All the dimers exhibit enantiotropic mesophases. The first member of the dimers having the C_4 central spacer exhibit only the chiral nematic (N*) mesophase, while the higher homologues also show smectic A (SmA) and twist grain boundary (TGB) mesophases. The dimers of the other series containing the C_5 central spacer also have stable SmA, TGB and N* mesophases, except for the first which does not show the TGB phase. Both series of compounds show a weak odd–even effect with terminal alkyl chain substitution, while the spacer length has a marked influence on the phase transition temperatures.

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1. Introduction

In recent years liquid crystal dimers (also known as dimesogens), composed of either two identical (symmetric) or non-identical (non-symmetric) mesogenic units connected via a flexible central spacer, have attracted attention not only because they are regarded as model compounds for polymeric liquid crystals but also due to their inherently interesting liquid crystalline properties [1]. There are remarkable differences in the behaviour of symmetric and non-symmetric dimers. In particular, chiral dimers possessing a cholesterly ester unit as the chiral entity joined to an aromatic mesogenic unit such as, for example, Schiff's base, azo benzene, stilbene, benzoate ester [2, 3], tolan [4, 5], salicylaldimine [6], or biphenyl [7, 8] through a polymethylene spacer, have shown interesting thermal behaviour.

For example, non-symmetric dimer formed by joining a cholesterly ester moiety to a Schiff's base through an *n*-pentyl (C_5) spacer exhibits a rich polymorphic sequence including an incommensurate smectic A mesophase [2*b*]. Further studies on similar types of compounds showed that the length of the spacer and the molecular structure of the aromatic mesogenic segment are more important for the observation of an incommensurate phase than for the formation of other mesophases such as blue phases (BP), the twist grain boundary (TGB) phase and the chiral smectic C phase [2*c*–*e*]. In order to understand structure–property relationships in these non-symmetric dimers and to explore the possibilty of obtaining incommensurate mesophases, dimers were prepared by attaching different types of chiral or achiral Schiff's base units to the cholesterly ester group via a *n*-pentyl spacer. These dimers exhibit smectic A (SmA), TGB and chiral nematic (N*) mesophases [3] revealing the sensitivity of mesogenic behaviour to the structure of the aromatic mesogenic segment. The disappointing feature of that study was that these molecules were thermally unstable and moisture sensitive owing to the presence of the imine group.

In view of this, we focused attention on the design and synthesis of dimers that are both thermally and hydrolytically stable and which may exhibit interesting smectic mesophases. Working in this direction, we attached an achiral or a chiral tolan-based moiety to a cholesterly ester unit via a central paraffinic spacer. The resulting non-symmetric dimers exhibited N* [4] or SmA [5] behaviour over a wide temperature range. We have also used the salicylaldimine [*N*-(*N*-2-hydroxy-4-alkoxybezylidene)aniline] segment as the aromatic group. The dimers obtained showed SmC*, SmA, TGB and N* mesophases [6] without any sign of frustrated smectic mesophases.

Alternatively, biphenyl may be used as the aromatic moiety, as it closely resembles the aromatic cores mentioned in the proceeding discussion. To date, there have been two reports in which the 4-cyanobiphenyl-4′-oxy unit [7] or the alkyl 4′-biphenyloxy-4-carboxylate

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core [8] has been linked to a cholesterly ester unit through paraffinic spacers. Both investigations revealed that the mesomorphic behaviour of these systems is sensitive to the parity of the spacer and nature of the terminal substituent on the biphenyl segment. It is noteworthy, that one of these non-symmetric dimers containing the alkyl 4′-biphenyloxy-4-carboxylate unit exhibits three smectic phases in addition to the N* mesophase. This result prompted us to vary the terminal substitution on the biphenyl ring, and specifically we have now synthesized non-symmetric dimers in which a cholesterly ester unit is connected to 4-*n*-alkoxy-biphenyl-4′-oxy cores through either an *n*-butyl or an *n*-pentyl central spacer and have determined their liquid crystalline properties.

2. Experimental

2.1. *General information*

Cholesterol and 1-bromoalkanes were obtained from Aldrich, while 4,4′-dihydroxybiphenyl was obtained from Lancaster. Acetone, 2-butanone (HPLC grade) and potassium carbonate were obtained from a local source; the solvents were used as received, whereas potassium carbonate was dried following a standard procedure. Column chromatographic separations were performed using silica gel (100–200 mesh). Thin layer chromatography was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge 60, F_{254}). IR spectra were recorded using a Perkin Elmer Spectrum 1000 FTIR spectrometer. ^{1}H NMR spectra were recorded using either a Bruker AMX-400 (400 MHz), a Bruker Aveance series DPX-200 (200 MHz) or a JEOL 300 (300 MHz) spectrometer. Mass spectra were recorded on a JEOL JMS-600H spectrometer. Mesophases were identified and their transition temperatures determined using a polarizing optical microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90). The enthalpies of the phase transitions were measured using a differential scanning calorimeter (Perkin Elmer DSC7). The melting transitions of non-mesogenic compounds were recorded using the microscope equipped with a hot-stage.

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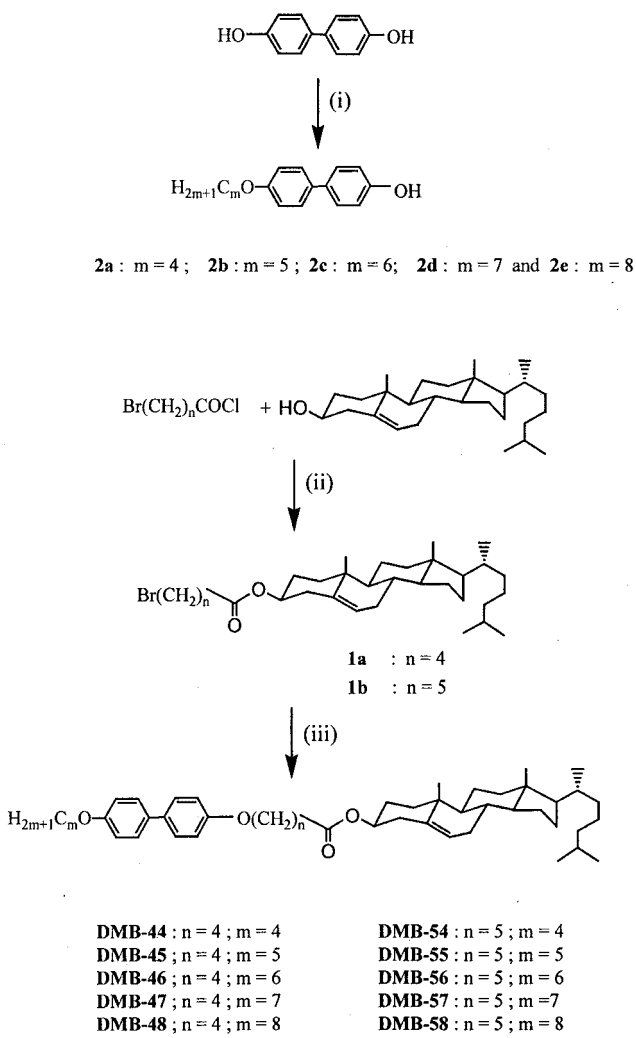
2.2. *Synthesis*

The non-symmetric dimers and their intermediates were synthesized as outlined in the scheme. 4-*n*-Alkoxy-4′-hydroxybiphenyls (**2a–e**) were prepared by the controlled O-alkylation of 4,4′-dihydroxybiphenyl with *n*-alkylbromides under mild basic reaction conditions using 2-butanone as a solvent. The cholesterly 5-bromopentanoate (**1a**) and cholesterly 6-bromohexanoate (**1b**) were synthesized by treating commercial optically pure cholesterol with 5-bromopetanoyl or 6-bromohexanoyl chloride, respectively [8]. Upon treating these bromo-



Scheme. Synthetic route to the non-symmetric dimers. (i) Anhyd. K_2CO_3, 1-*n*-bromoalkane, 2-butanone reflux, 24 h; (ii) pyridine-THF, rt, 24 h; (iii) 4-*n*-alkyloxy-4′-hydroxybiphenyl (**2a–e**), acetone, anhyd. K_2CO_3 reflux, 24 h.

substituted compounds, **1a** and **1b**, with the hydroxybiphenyls **2a–e** the non-symmetric dimers were obtained in reasonably good yields. The molecular structures of the dimers and their intermediates were confirmed by spectroscopic analyses.

2.2.1. *4-n-Alkoxy-4′-hydroxybiphenyls (**2a–e**)*

These intermediates were all prepared following the same general synthetic procedure. Thus, a flask equipped with a magnetic stirrer, reflux condenser and argon inlet was charged with 2-butanone (40 ml), anhydrous potassium carbonate (7.4 g, 53.5 mmol, 5 equiv.), 4,4′-dihydroxybiphenyl (2 g, 10.7 mmol, 1 equiv.) and 1-*n*-bromoalkane (4.5 mmol, 0.4 equiv.). The reaction mixture was heated at reflux for 24 h and was filtered hot through a celite bed. The filtrate was removed under

vacuum to get a solid residue, which was poured into water (50 ml). The off-white solid that separated was collected by filtration. It was purified by column chromatography using silica gel (100–200 mesh). Elution, first with hexane followed by a mixture of 5% EtOAc–hexanes afforded a colourless solid, which was further purified by repeated recrystallization from absolute ethanol to obtain the product in 30–40% yield.

*4-n-Butyloxy-4′-hydroxybiphenyl (**2a**).* $R_f = 0.45$ (30% EtOAc–hexanes), white solid, m.p. 168–168.5°C, yield 0.92 g (35%). IR (KBr pellet): γ_{max} 3369, 2957, 2916, 2871, 1611, 1597, 1248 and 815 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): 7.45 (d, $J = 8.8$ Hz, 2H, Ar), 7.42 (d, $J = 8.72$ Hz, 2H, Ar), 6.94 (d, $J = 8.86$ Hz, 2H, Ar), 6.87 (d, $J = 8.74$ Hz, 2H, Ar), 4.79 (s, 1H, −OH), 3.99 (t, $J = 6.47$ Hz, 2H, $-OCH_2-$), 2.0–1.3 (m, 4H, $2 \times -CH_2-$) and 0.98 (t, $J = 7.28$ Hz, 3H, $-CH_3$). FAB Mass: 242.1 $[M^+]$ (calculated for $C_{16}H_{18}O_2$).

*4-n-Pentyloxy-4′-hydroxybiphenyl (**2b**).* $R_f = 0.45$ (30% EtOAc–hexanes), white solid, m.p. 158–158.5°C, yield 0.85 g (31%). IR (KBr pellet): γ_{max} 3350, 2956, 2933, 2868, 1611, 1502, 1250 and 813 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): 7.45 (d, $J = 8.72$ Hz, 2H, Ar), 7.42 (d, $J = 8.64$ Hz, 2H, Ar), 6.94 (d, $J = 8.76$ Hz, 2H, Ar), 6.87 (d, $J = 8.62$ Hz, 2H, Ar), 4.80 (s, 1H, −OH), 3.98 (t, $J = 6.56$ Hz, 2H, $-OCH_2-$), 2.0–1.1 (m, 6H, $3 \times -CH_2-$) and 0.93 (t, $J = 7.12$ Hz, 3H, $-CH_3$). FAB Mass: 256.1 $[M^+]$ (calculated for $C_{17}H_{20}O_2$).

*4-n-Hexyloxy-4′-hydroxybiphenyl (**2c**).* $R_f = 0.46$ (30% EtOAc–hexanes), white solid, m.p. 156–157°C, yield 1.14 g (39.4%). IR (KBr pellet): γ_{max} 3294, 2954, 2933, 2868, 1609, 1503, 1249 and 822 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): 7.44 (d, $J = 8.76$ Hz, 2H, Ar), 7.42 (d, $J = 8.66$ Hz, 2H, Ar), 6.94 (d, $J = 8.8$ Hz, 2H, Ar), 6.87 (d, $J = 8.68$ Hz, 2H, Ar), 4.79 (s, 1H, −OH), 3.98 (t, $J = 6.54$ Hz, 2H, $-OCH_2-$), 2.0–1.25 (m, 8H, $4 \times -CH_2$) and 0.91 (t, $J = 7.12$ Hz, 3H, $-CH_3$). FAB Mass: 270.0 $[M^+]$ (calculated for $C_{18}H_{22}O_2$).

*4-n-Heptyloxy-4′-hydroxybiphenyl (**2d**).* $R_f = 0.46$ (30% EtOAc–hexanes), white solid, m.p. 154–155°C, yield 1.19 g (39%). IR (KBr pellet): γ_{max} 3381, 2954, 2930, 2856, 1609, 1503, 1249 and 814 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): 7.44 (d, $J = 8.74$ Hz, 2H, Ar), 7.42 (d, $J = 8.62$ Hz, 2H, Ar), 6.94 (d, $J = 8.78$ Hz, 2H, Ar), 6.87 (d, $J = 8.66$ Hz, 2H, Ar), 4.77 (s, 1H, −OH), 3.98 (t, $J = 6.55$ Hz, 2H, $-OCH_2-$), 2.0–1.25 (m, 10H, $5 \times -CH_2$) and 0.86 (t, $J = 7.12$ Hz, 3H, $-CH_3$). FAB Mass: 284.0 $[M^+]$ (calculated for $C_{19}H_{24}O_2$).

*4-n-Octyloxy-4′-hydroxybiphenyl (**2e**).* $R_f = 0.46$ (30% EtOAc–hexanes), white solid, m.p. 153–154°C, yield 1.16 g (36.4%). IR (KBr pellet): γ_{max} 3305, 2920, 2854, 1609, 1503, 1251 and 822 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): 7.44 (d, $J = 8.66$ Hz, 2H, Ar), 7.42 (d, $J = 8.54$ Hz, 2H, Ar), 6.94 (d, $J = 8.74$ Hz, 2H, Ar), 6.87 (d, $J = 8.56$ Hz, 2H, Ar), 4.78 (s, 1H, −OH), 3.98 (t, $J = 6.55$ Hz, 2H, $-OCH_2-$), 2.0–1.25 (m, 12H, $6 \times -CH_2$) and 0.88 (t, $J = 7.12$ Hz, 3H, $-CH_3$). FAB Mass: 298.0 $[M^+]$ (calculated for $C_{20}H_{26}O_2$).

2.2.2. *Cholesterly 5/6-[4-(4′-n-alkoxy)biphenyloxy]-alkanoates (DMB-4,4 to DMB-4,8 and DMB-5,4 to DMB-5,8)*

The non-symmetric dimers were all synthesized following the same general synthetic procedure. Thus, a 100 ml flask equipped with water condenser and argon inlet, was charged with acetone (HPLC grade, 50 ml), anhydrous potassium carbonate (5 g, 36.4 mmol, 10 equiv.), 4-*n*-alkoxy-4′-hydroxybiphenyl (**2a–e**) (5.46 mmol, 1.5 equiv.) and cholesterly 5/6-bromoalkanoates (**1a**,**b**) (3.64 mmol, 1 equiv.), and then flushed with argon for some time. After closing the neck with a septum, the reaction mixture was heated at reflux for 24 h with vigorous stirring and filtered hot through a celite bed. The filtrate was evaporated under vaccum and the pale yellow solid obtained was poured into ice-cold water, and collected by filtration. The solid obtained was dissolved in $CHCl_3$ (40 ml) and the resulting solution washed with a 5% aqueous NaOH (20 ml × 2), 0.1M HCl (20 ml × 2), 5% aqueous NaOH (10 ml × 2), water (10 ml × 2), brine and then dried over anhydrous Na_2SO_4. Evaporation of the solvent gave an off-white solid which was purified by column chromatography using silica gel (100–200 mesh). Elution with a mixture of 5% EtOAc–hexanes yielded a white solid which was purified further by repeated recrystallization (4 times) from a mixture of absolute ethanol–CH_2Cl_2 (9 : 1).

Cholesterly 5-[4-(4′-n-butyloxy)biphenyloxy]pentanoate (DMB-4,4) $R_f = 0.40$ (10% EtOAc–hexanes), white solid, yield 1.76 g (68%). IR (KBr pellet): γ_{max} 2936, 2869, 1735, 1606 and 1501 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 7.45 (d, $J = 9$ Hz, 4H, Ar), 6.95 (d, $J = 2.4$ Hz, 2H, Ar), 6.92 (d, $J = 2.1$ Hz, 2H, Ar), 5.37 (brd, $J = 4.2$ Hz, 1H, olefinic), 4.61 (m, 1H, $-CH-O-CO-$), 4.0 (m, 4H, $2 \times -OCH_2-$), 2.31 (m, 4H, $2 \times$ allylic methylene), 2.01–0.94 (m, 37H, $1 \times CH_3-$, $14 \times -CH_2-$, $6 \times -CH-$), 1.0 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.6$ Hz, 3H, $-CH_3$), 0.86 (d, $J = 3.0$ Hz, 6H, $2 \times -CH_3$) and 0.67 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): 172.89, 158.25, 158.0, 139.66, 133.49, 133.28, 127.67, 122.66, 114.73, 73.9, 67.77, 67.45, 56.69, 56.13, 50.01, 42.32, 39.73, 39.52, 38.15, 36.99, 36.60, 36.19, 35.80, 34.31, 31.90, 31.85, 31.38, 28.69, 28.24, 28.02, 27.82, 24.29, 23.84, 22.82, 22.57, 21.75, 21.03, 19.32, 19.28, 18.72, 13.87 and 11.86. FAB Mass: 710.3 $[M^+]$ (calculated for $C_{48}H_{70}O_4$).

Cholesterly 5-[4-(4′-n-pentyloxy)biphenyloxy]pentanoate (DMB-4,5). $R_f = 0.42$ (10% EtOAc–hexanes), white solid, yield 1.66 g (63%). IR (KBr pellet): γ_{max} 2935, 2868, 1732, 1607 and 1501 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz):

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7.45 (d, $J = 8.68$ Hz, 4H, Ar), 6.94 (d, $J = 2.84$ Hz, 2H, Ar), 6.92 (d, $J = 2.8$ Hz, 2H, Ar), 5.37 (brd, $J = 4.21$ Hz, 1H, olefinic), 4.61 (m, 1H, $-CH-O-CO-$), 4.0 (m, 4H, $2 \times -OCH_2-$), 2.31 (m, 4H, $2 \times$ allylic methylene), 2.1–0.95 (m, 39H, $1 \times CH_3-$, $15 \times -CH_2-$, $6 \times -CH-$), 1.02 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.4$ Hz, 3H, $-CH_3$), 0.87 (d, $J = 1.72$ Hz, 3H, $-CH_3$), 0.85 (d, $J = 1.72$ Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). FAB Mass: 724.2 [M^+] (calculated for $C_{49}H_{72}O_4$).

Cholesterly 5-[4-(4′-n-hexyloxy)biphenyloxy]pentanoate (DMB-4,6). $R_f = 0.42$ (10% EtOAc–hexanes), white solid, yield 2.3 g (86%). IR (KBr pellet): γ_{max} 2933, 2868, 1732, 1607 and 1501 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 7.45 (d, $J = 8.6$ Hz, 4H, Ar), 6.94 (d, $J = 2.84$ Hz, 2H, Ar), 6.92 (d, $J = 2.8$ Hz, 2H, Ar), 5.36 (brd, $J = 4.21$ Hz, 1H, olefinic), 4.62 (m, 1H, $-CH-O-CO-$), 4.0 (m, 4H, $2 \times -OCH_2-$), 2.31 (m, 4H, $2 \times$ allylic methylene), 2.1–0.96 (m, 41H, $1 \times CH_3-$, $16 \times -CH_2-$, $6 \times -CH-$), 1.0 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.4$ Hz, 3H, $-CH_3$), 0.87 (d, $J = 1.68$ Hz, 3H, $-CH_3$), 0.85 (d, $J = 1.64$ Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). FAB Mass: 738.0 [M^+] (calculated for $C_{50}H_{74}O_4$).

Cholesteryl 5-[4-(4′-n-heptyloxy)biphenyloxy] pentanoate (DMB-4,7). $R_f = 0.42$ (10% EtOAc–hexanes), white solid, yield 1.7 g (61%). IR (KBr pellet): γ_{max} 2935, 2870, 1738, 1607 and 1501 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 7.45 (d, $J = 8.48$ Hz, 4H, Ar), 6.94 (d, $J = 2.64$ Hz, 2H, Ar), 6.92 (d, $J = 2.6$ Hz, 2H, Ar), 5.37 (brd, $J = 4.21$ Hz, 1H, olefinic), 4.61 (m, 1H, $-CH-O-CO-$), 4.01 (m, 4H, $2 \times -OCH_2-$), 2.31 (m, 4H, $2 \times$ allylic methylene), 2.1–0.96 (m, 43H, $1 \times CH_3-$, $17 \times -CH_2-$, $6 \times -CH-$), 1.0 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.52$ Hz, 3H, $-CH_3$), 0.87 (d, $J = 1.76$ Hz, 3H, $-CH_3$), 0.85 (d, $J = 1.72$ Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). FAB Mass: 752.5 [M^+] (calculated for $C_{51}H_{76}O_4$).

Cholesteryl 5-[4-(4′-n-octyloxy)biphenyloxy]pentanoate (DMB-4,8). $R_f = 0.44$ (10% EtOAc–hexanes), white solid, yield 1.9 g (68%). IR (KBr pellet): γ_{max} 2934, 2868, 1729, 1608 and 1568 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 7.45 (d, $J = 8.64$ Hz, 4H, Ar), 6.94 (d, $J = 2.56$ Hz, 2H, Ar), 6.92 (d, $J = 2.52$ Hz, 2H, Ar), 5.35 (brd, $J = 4.12$ Hz, 1H, olefinic), 4.61 (m, 1H, $-CH-O-CO-$), 4.01 (m, 4H, $2 \times -OCH_2-$), 2.31 (m, 4H, $2 \times$ allylic methylene), 2.1–0.92 (m, 45H, $1 \times CH_3-$, $18 \times -CH_2-$, $6 \times -CH-$), 1.0 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.48$ Hz, 3H, $-CH_3$), 0.87 (d, $J = 1.52$ Hz, 3H, $-CH_3$), 0.85 (d, $J = 1.64$ Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). FAB Mass: 766.0 [M^+] (calculated for $C_{52}H_{78}O_4$).

Cholesterly 6-[4-(4′-n-butyloxy)biphenyloxy]hexanoate (DMB-5,4) $R_f = 0.36$ (10% EtOAc–hexanes), white solid, yield 1.7 g (67%). IR (KBr pellet): γ_{max} 2937, 2868, 1734, 1607 and 1501 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 7.45 (d, $J = 8.72$ Hz, 4H, Ar), 6.94 (d, $J = 4.80$ Hz, 2H, Ar), 6.92 (d, $J = 4.80$ Hz, 2H, Ar), 5.37 (brd, $J = 4.21$ Hz, 1H, olefinic), 4.62 (m, 1H, $-CH-O-CO-$), 4.0 (m, 4H, $2 \times -OCH_2-$), 2.31 (t, $J = 7.4$ Hz, 4H, $2 \times$ allylic methylene), 2.1–0.96 (m, 39H, $1 \times CH_3-$, $15 \times -CH_2-$, $6 \times -CH-$), 1.0 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.52$ Hz, 3H, $-CH_3$), 0.87 (d, $J = 1.72$ Hz, 3H, $-CH_3$), 0.85 (d, $J = 1.72$ Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): 173.05, 158.24, 158.1, 139.67, 133.4, 133.2, 127.6, 122.6, 114.7, 73.8, 67.75, 67.69, 56.7, 56.1, 50.0, 42.3, 39.7, 39.52, 38.15, 36.98, 36.59, 36.18, 35.79, 34.59, 31.9, 31.85, 31.38, 28.98, 28.23, 28.01, 27.81, 25.63, 24.80, 24.29, 23.82, 22.82, 22.57, 21.03, 19.32, 19.27, 18.71, 13.87 and 11.85. FAB Mass: 724.2 [M^+] (calculated for $C_{49}H_{72}O_4$).

Cholesteryl 6-[4-(4′-n-pentyloxy)biphenyloxy]hexanoate (DMB-5,5). $R_f = 0.40$ (10% EtOAc–hexanes), white solid, yield 1.6 g (61%). IR (KBr pellet): γ_{max} 2937, 2867, 1739, 1608 and 1501 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 7.45 (d, $J = 8.6$ Hz, 4H, Ar), 6.94 (d, $J = 4.20$ Hz, 2H, Ar), 6.92 (d, $J = 4.60$ Hz, 2H, Ar), 5.37 (brd, $J = 4.18$ Hz, 1H, olefinic), 4.62 (m, 1H, $-CH-O-CO-$), 4.0 (m, 4H, $2 \times -OCH_2-$), 2.31 (t, $J = 7.46$ Hz, 4H, $2 \times$ allylic methylene), 2.1–0.96 (m, 41H, $1 \times CH_3-$, $16 \times -CH_2-$, $6 \times -CH-$), 1.0 (s, 3H, $-CH_3$), 0.92 (d, $J = 6.44$ Hz, 3H, $-CH_3$), 0.87 (d, $J = 1.52$ Hz, 3H, $-CH_3$), 0.85 (d, $J = 1.52$ Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). FAB Mass: 738.0 [M^+] (calculated for $C_{50}H_{74}O_4$).

Cholesteryl 6-[4-(4′-n-hexyloxy)biphenyloxy]hexanoate (DMB-5,6). $R_f = 0.42$ (10% EtOAc–hexanes), white solid, yield 2 g (74%). IR (KBr pellet): γ_{max} 2938, 2866, 1736, 1607 and 1500 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 7.45 (d, $J = 8.6$ Hz, 4H, Ar), 6.94 (d, $J = 4.32$ Hz, 2H, Ar), 6.92 (d, $J = 4.40$ Hz, 2H, Ar), 5.37 (brd, $J = 4.18$ Hz, 1H, olefinic), 4.62 (m, 1H, $-CH-O-CO-$), 4.0 (m, 4H, $2 \times -OCH_2-$), 2.31 (t, $J = 7.40$ Hz, 4H, $2 \times$ allylic methylene), 2.1–0.96 (m, 43H, $1 \times CH_3-$, $17 \times -CH_2-$, $6 \times -CH-$), 1.0 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.24$ Hz, 3H, $-CH_3$), 0.87 (d, $J = 1.72$ Hz, 3H, $-CH_3$), 0.85 (d, $J = 1.72$ Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). FAB Mass: 752.2 [M^+] (calculated for $C_{51}H_{76}O_4$).

Cholesteryl 6-[4-(4′-n-heptyloxy)biphenyloxy]hexanoate (DMB-5,7). $R_f = 0.42$ (10% EtOAc–hexanes), white solid, yield 1.86 g (68%). IR (KBr pellet): γ_{max} 2937, 2867, 1735, 1606 and 1500 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 7.45 (d, $J = 8.68$ Hz, 4H, Ar), 6.94 (d, $J = 4.12$ Hz, 2H, Ar), 6.92 (d, $J = 4.2$ Hz, 2H, Ar), 5.37 (brd, $J = 4.32$ Hz, 1H, olefinic), 4.62 (m, 1H, $-CH-O-CO-$), 4.0 (m, 4H, $2 \times -OCH_2-$), 2.31 (t, $J = 7.40$ Hz, 4H, $2 \times$ allylic methylene), 2.1–0.96 (m, 45H, $1 \times CH_3-$, $18 \times -CH_2-$, $6 \times -CH-$), 1.0 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.50$ Hz, 3H, $-CH_3$), 0.87 (d, $J = 1.6$ Hz, 3H, $-CH_3$), 0.85 (d, $J = 1.68$ Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). FAB Mass: 766.4 [M^+] (calculated for $C_{52}H_{78}O_4$).

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Cholesteryl 6-[4-(4′-n-octyloxy)biphenyloxy]hexanoate (DMB-5,8). R_f = 0.44 (10% EtOAc–hexanes), white solid, yield 2 g (73%). IR (KBr pellet): γ_{max} 2934, 2867, 1735, 1606 and 1501 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 7.45 (d, J = 8.7 Hz, 4H, Ar), 6.93 (d, J = 4.08 Hz, 2H, Ar), 6.92 (d, J = 4.12 Hz, 2H, Ar), 5.37 (brd, J = 4.32 Hz, 1H, olefinic), 4.62 (m, 1H, −CH−O−CO−), 4.0 (m, 4H, 2 × $-OCH_2-$), 2.30 (t, J = 7.43 Hz, 4H, 2 × allylic methylene), 2.1–0.96 (m, 47H, 1 × CH_3-, 19 × $-CH_2-$, 6 × −CH−), 1.0 (s, 3H, $-CH_3$), 0.91 (d, J = 6.48 Hz, 3H, $-CH_3$), 0.87 (d, J = 1.72 Hz, 3H, $-CH_3$), 0.85 (d, J = 1.76 Hz, 3H, $-CH_3$) and 0.67 (s, 3H, $-CH_3$). FAB Mass: 780.1 [M^+] (calculated for $C_{53}H_{80}O_4$).

3. Results and discussion

As can be seen from the table, all the dimers exhibit enantiotropic mesophases. The non-symmetric dimer DMB-4,4 containing a butyl spacer, exhibits only an N* mesophase and shows the characteristic oily streak texture which on slight shearing changes to a planar texture on an ordinary glass plate. The higher homologues DMB-4,5, DMB-4,6, DMB-4,7, and DMB-4,8 show SmA and TGB phases in addition to the N* mesophase. The SmA mesophase has been identified based on the microscopic observation of a characteristic focal-conic texture using slides treated for planar orientation, and a dark field of view with slides treated for homeotropic orientation. The TGB phase gave a filament texture on heating from a homeotropic SmA phase. In compounds with a very narrow TGB phase temperature range, the N* and SmA phases coexisted with the TGB phase; this was evident from the fact that the textures corresponding to these three mesophases appear simultaneously for a short time. The dimers DMB-5,5, DMB-5,6, DMB-5,7 and DMB-5,8 of the other series, in which two non-identical mesogens are separated by pentyl spacer, also show SmA, TGB and N* mesophases. The first member, DMB-5,4, shows only SmA and N* mesophases. As representative examples, the DSC traces for both the heating and cooling cycles obtained at a rate of 5°C min^{-1} for DMB-4,4 are shown in figure 1.

In both series a slight odd–even effect on varying the terminal alkyl chain length (m) is seen in the clearing temperatures. The compounds with a butyl spacer show considerably lower clearing temperatures (figure 2) than the dimers with a pentyl spacer (figure 3). The same is true for Cr–SmA, SmA–TGB and TGB–N* transition temperatures. Similar observations have been made for dimers composed of a cholesterly unit and a biphenyl segment which differ from our dimers in the type of the terminal substituent on the biphenyl unit [7, 8]. In contrast to the behaviour of the dimers we have synthesized, however, these materials do not exhibit the

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Table. Phase transition temperatures[a] (in °C) and enthalpies (in J g^{-1}) of the non-symmetric dimers. The enthalpies are in square brackets. Cr = crystal; SmA = smectic A; TGB = twist grain boundary; N* = chiral nematic; I = isotropic liquid.

Dimer	n	m	Cr	Heating; Cooling	SmA	Heating; Cooling	TGB	Heating; Cooling	N*	Heating; Cooling	I
DMB-4,4	4	4	•	104.6; 95.0 [25.8; 26.4]	—		—		•	153.05; 152.8 [1.41; 1.50]	•
DMB-4,5	4	5	•	119.6; 104.9 [49.5; 45.1]	•	124.4; 123.3	•	129.6; 127.3 [0.7; 0.5][b]	•	150.0; 147.8 [2.1; 2.5]	•
DMB-4,6	4	6	•	127.2; 100.0 [67.7; 57.1]	•	136.1; 135.7	•	137.6; 136.2 [1.5; 1.4][b]	•	150.7; 149.0 [2.2; 2.3]	•
DMB-4,7	4	7	•	112.3; 84.2 [51.6; 35.1]	•	139.4; 138.0	•	140.5; 138.8 [1.7; 1.7][b]	•	146.1; 144.4 [1.8; 1.6]	•
DMB-4,8	4	8	•	107.8; 69.3 [50.0; 34.1]	•	144.7; 144.0	•	145.2; 144.3 [2.6; 2.3][b]	•	147.8; 147.2 [1.5; 1.9]	•
DMB-5,4	5	4	•	116.6; 97.7 [30.9; 27.3]	•	166.5; 165.5 [1.3; 1.8]	—		•	190.6; 190.0 [6.5; 5.4]	•
DMB-5,5	5	5	•	145.2; 98.6 [47.1; 29.5]	•	170.8; 164.8	•	171.0; 165.0 [2.0; 1.7][b]	•	188.5; 185.2 [6.5; 4.9]	•
DMB-5,6	5	6	•	134.3; 108.8 [40.6; 38.4]	•	158.3; 157.9	•	164.3; 163.5 [0.8; 0.6][b]	•	182.1; 182.0 [6.2; 5.8]	•
DMB-5,7	5	7	•	139.7; 106.8 [37.2; 38.5]	•	167.2; 167.2	•	168.0; 167.8 [1.1; 1.1][b]	•	179.4; 179.0 [5.5; 5.8]	•
DMB-5,8	5	8	•	111.5; 82.9 [31.6; 24.0]	•	172.2; 171.8	•	172.4; 172.0 [1.34; 0.9][b]	•	177.5; 176.8 [4.0; 4.3]	•

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

[b] Although SmA–TGB and TGB–SmA transition was observed under the microscope, it was not resolved in DSC scan. Hence the enthalpy value represents the combined enthalpy for SmA–TGB and TGB–SmA transitions.

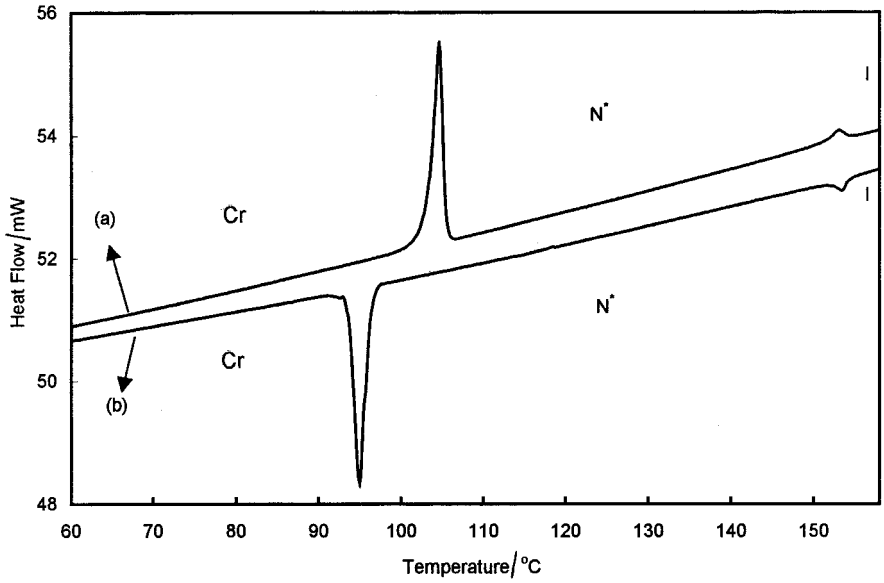

Figure 1. DSC traces obtained for DMB-4,4 at a rate of 5°C min^{-1}: (*a*) first heating and (*b*) first cooling.

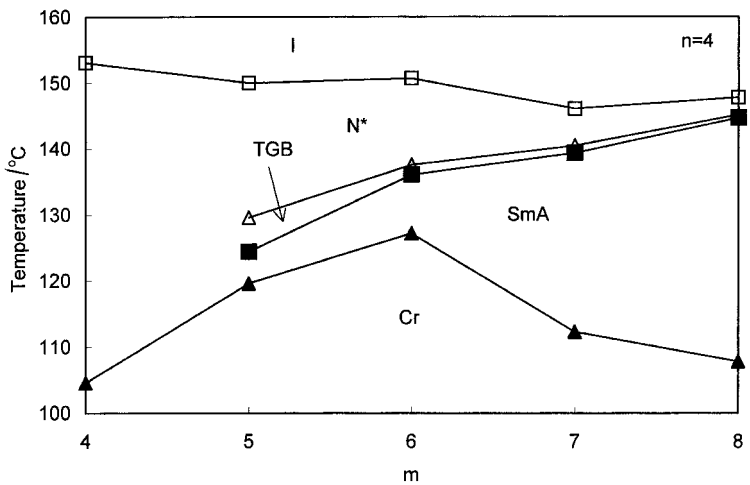

Figure 2. Dependence of the transition temperatures on the number of methylene units in the terminal alkyl chain for the nonsymmetrical dimers DMB-4,*m*. ▲ Cr–SmA ■ SmA–TGB △ TGB–N* □ N*–I.

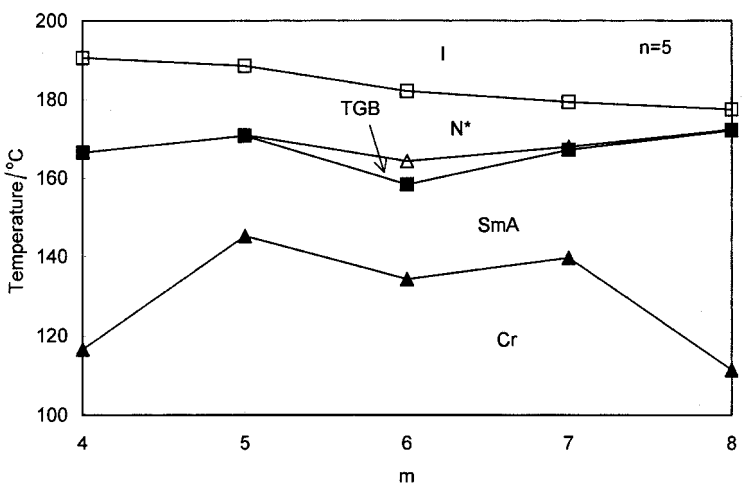

Figure 3. Dependence of the transition temperatures on the number of methylene units in the terminal alkyl chain for the nonsymmetric dimers DMB-5,*m*. ▲ Cr–SmA ■ SmA–TGB △ TGB–N* □ N*–I.

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TGB phase, showing the sensitivity of mesomorphic behaviour to the nature of the terminal substituent on the biphenyl segment.

In summary, we have synthesized chiral non-symmetric dimeric liquid crystalline compounds composed of a cholesterly ester unit, as the chiral entity, and a biphenyl core connected via a central alkylene spacer. Both the spacer and terminal chain lengths have been varied with a view to stabilizing different smectic mesophases and understanding structure–property relationships. Our study reveals that the present structural combination does not promote the formation of different smectic mesophases other than the SmA phase. Furthermore, it appears that the length of the terminal alkyl chain hardly influences the mesophase formation as all the members, except for the first member of both series exhibit SmA, TGB and N* phases. On the other hand, the parity of the spacer chain length strongly affects all the phase transition temperatures. These results are useful in gaining a better understanding of the relationship between chemical structure and physical properties in chiral non-symmetric dimers.

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