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Mesogenic Unsymmetric dimers containing cholesteryl ester and tolane moieties

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Among unsymmetric oligomesogens, chiral dimers formed by connecting a cholesteryl ester fragment with various aromatic mesogenic cores through a polymethylene spacer have been attracting much attention due to their remarkable thermal behaviour. In particular, dimers containing a diphenylacetylene segment having an alkoxy chain have shown interesting mesomorphic behaviour. In view of this a new series of unsymmetric dimers consisting of a diphenylacetylene moiety having an alkyl chain and a cholesteryl ester unit joined through a paraffinic spacer have been synthesized and their liquid crystalline properties characterized. The lengths of the central methylene spacer (C_3, C_4, C_5 and C_7) as well as that of the alkyl chain (*n*-butyl, *n*-pentyl, *n*-hexyl and *n*-heptyl) have been varied to establish structure–property relationships. These investigations have revealed that all the dimers exhibit smectic A, twist grain boundary and chiral neamtic (N*) phases with the exception of one of the dimers for which only the N* phase was observed. Some differences in the mesomorphic properties of the unsymmetric dimers containing odd or even parity methylene spacers have been observed. The majority of dimers having an even (C_4) parity paraffinic spacer show a blue phase while the dimers with odd (C_3, C_5 and C_7) parity spacers exhibit the chiral smectic (SmC*) phase. In some cases, the SmC* phase exists well below (−60°C) and above room temperature.

1. Introduction

During the last two decades a considerable amount of research has been focused on non-conventional molecular structures, namely linear oligomeric liquid crystals (LOLCs), that are formed by joining two or more mesogenic (anisometric) cores in an end–end (axial) fashion by means of one or more methylene spacer/s [1]. The first class of LOLCs, dimers (also referred to as dimesogens or bimesogens), can be of two types: (a) symmetric dimers in which the two mesogenic units are identical and (b) unsymmetric dimesogens which contain two non-identical mesogenic cores [2]. Although symmetric dimers (twins) have been known for 75 years and were first reported by Vorlander in 1927 [3], their importance was overlooked until Griffin and Britt showed that dimers could be regarded as model compounds for the technologically important semi-flexible main chain liquid crystalline polymers [4]. Since then several studies of symmetric dimers have revealed that the liquid crystalline properties of these materials depend not only on both the parity (odd–even) and the length of the flexible central spacer, but also on the length of the terminal chains. By contrast, studies on unsymmetric compounds are less well advanced, although a few systems including chiral examples are known [2].

Recently chiral dimers containing a cholesteryl ester unit as the chiral entity joined to an aromatic mesogen through a polymethylene spacer have attracted attention as they show remarkable mesomorphic properties [5–9]. For example, Hardouin *et al.* reported that an unsymmetric dimer formed by joining a cholesteryl ester moiety to a Schiff's base unit through an *n*-pentyl (C_5) spacer exhibits a rich polymorphic sequence including an incommensurate smectic A (SmA_{ic}) phase [5*b*]. Further studies on similar types of compound showed that the length of the spacer and the molecular structure of the aromatic (non-cholesteryl mesogenic)

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core is more important for the occurrence of an incommensurate phase than for the appearance of other mesophases, such as the blue phases (BP), the twist grain boundary (TGB) phase and the chiral smectic C (SmC*) phase [5 *c–e*]. In order to understand structure–property relationships in these unsymmetric dimers, and the possibility of obtaining similar mesophases, we have synthesized different types of dimer in which either a chiral or an achiral Schiff's base unit was attached to the cholesteryl ester moiety through an *n*-pentyl spacer [6]. These compounds exhibit smectic A (SmA), TGB and chiral nematic (N*) mesophases, indicating the sensitivity of mesomorphic behaviour to the structure of the aromatic (non-cholesteryl) mesogenic segment in these systems. The disappointing factor was that these molecules were found to have irreproducible mesomorphic behaviour, which could be attributed to the presence of the imine linkage (–CH = N–) as this is known to be sensitive to heat and moisture.

To circumvent this difficulty, we have been engaged in the design and synthesis of unsymmetric dimers in which the aromatic mesogenic entity shows good resistance to heat and moisture and is connected to a cholesterol ester unit through an alkylene spacer. Recently we have attached an achiral or a chiral tolane (diphenylacetylene) fragment, to a cholesteryl ester unit via a central paraffinic spacer, and the resulting unsymmetric dimers exhibited the N* [7 *a*] or a SmA [7 *b*] phase over a wide temperature range but without any signs of the expected frustrated smectic mesophases. To extend this investigation, we prepared an unsymmetric dimer by joining a cholesteryl ester moiety to a 4-*n*-hexyloxytolane core through an *n*-pentyl (C_5) spacer. Interestingly this dimer showed a reentrant twist grain boundary phase (with smectic A blocks; TGB_A), and a newly discovered twist grain boundary phase (with smectic C* blocks; TGB_{C^*}) [8]. More recently Cha *et al.* have synthesized similar compounds but varying in the length of the alkoxy chains, and these are reported to show anomalies in the periodicity of different TGB structures [9]. Thus, small modifications of the molecular structure in these dimers can dramatically influence their thermotropic behaviour. This prompted us to design and synthesize new unsymmetric dimers in which an optically active cholesteryl unit is connected to a 4-*n*-alkyltolane instead of a 4-*n*-alkoxytolane moiety. Here we report the synthesis and characterization of the cholesteryl ω-[4-(4-*n*-alkylphenylethynyl)-phenoxy]alkanoates in which the lengths of both the central paraffinic spacer and the alkyl chain have been varied. These compounds are denoted **DTA-*n*,*R*** where ***n*** and ***R*** indicate the length of the spacer and terminal chain, respectively.

2. Experimental

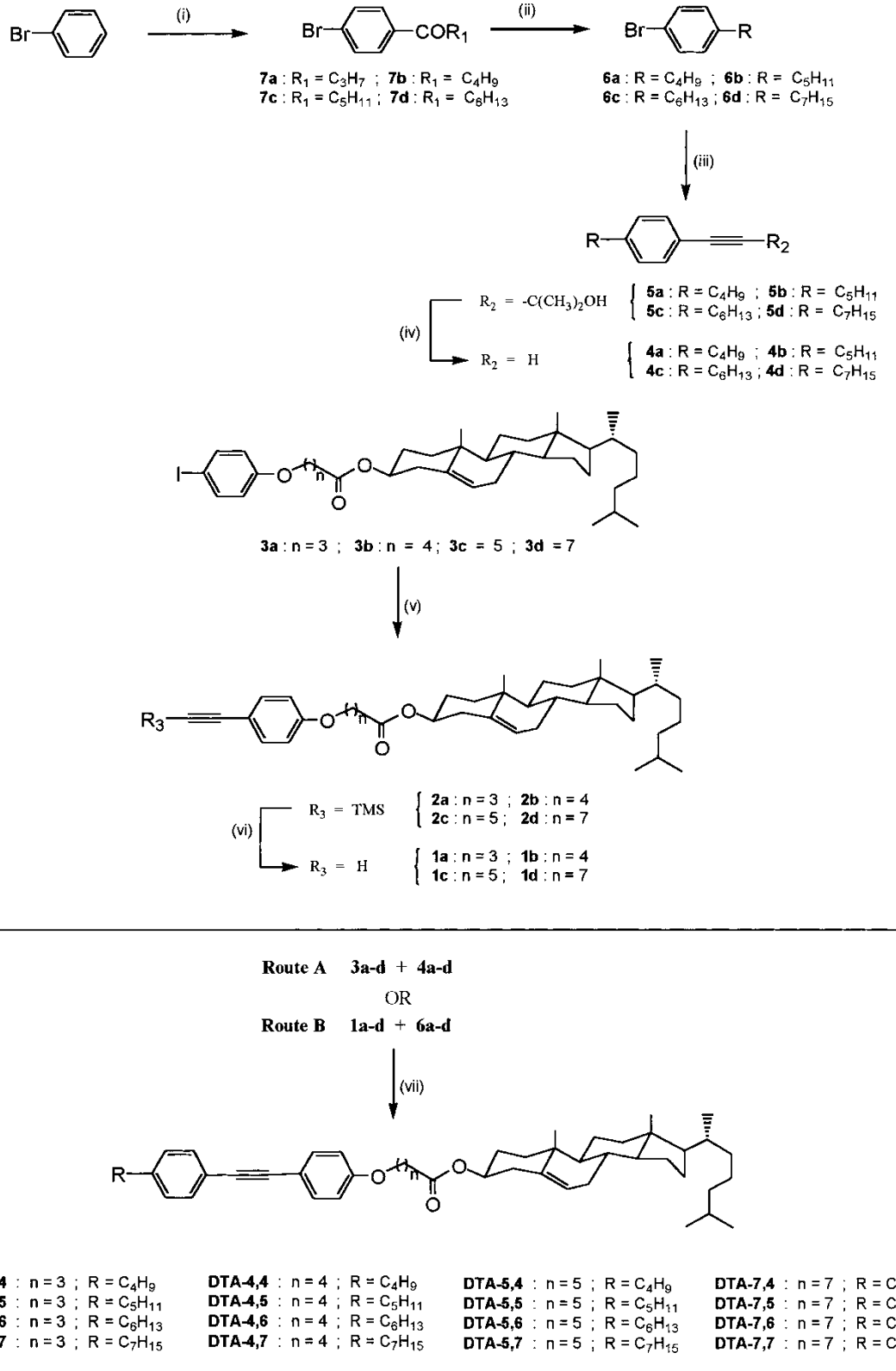
2.1. *Synthesis*

The unsymmetric dimers were synthesized as shown in the scheme. Initially all the dimers were prepared by synthetic route A but some, namely **DTA-3,4**, **DTA-4,5**, **DTA-5,6** and **DTA-7,7**, have also been obtained by route B in an effort to optimize the yield. Our synthetic studies revealed, however, that both routes give similar ranges of yields. The 4-*n*-alkylphenyl acetylenes (**4a–d**) were obtained following a literature procedure. Bromobenzene was first converted to various arylketones **7a–d** by treatment with different acid chlorides under Friedel–Crafts reaction conditions. The reduction of the arylketones gave 4-*n*-alkylbromobenzenes (**6a–d**), which were then converted to 4-*n*-phenylacetylenes (**4a–d**) via protected phenylacetylenes (**5a–d**). The other key intermediates, namely the cholesteryl (4-iodophenoxy)alkanoates (**3a–d**), were prepared by treating 4-iodophenol with cholesteryl bromo compounds as reported in the literature [7]. The iodo compounds **3a–d** were coupled with trimethylsilylacetylene using Pd(0) as catalyst to obtain the protected cholesteryl phenylacetylenes **2a–d** These protected acetylenes were treated with tetra-*n*-butylammonium fluoride to get the cholesteryl phenylacetylenes **1a–d** in quantitative yields [10]. By route A, the dimers were obtained by reacting the cholesteryl iodo compounds **3a–d** with the 4-*n*-alkylphenylaceylenes (**6a–d**) under Pd(0)-Cu(I)-catalysed reaction conditions; whereas in route B, the cholesteryl phenylacetylenes **1a–d** were coupled with 4-*n*-alkylbromobenzenes (**4a–d**) under similar reaction conditions.

2.2. *General information*

Bromobenzene, butyric acid, valeric acid, caproic acid, heptanoic acid, common solvents and reagents were obtained from local sources. Solvents were purified and dried following standard procedures. Cholesterol, trimethylsilylacetylene, 8-bromooctanoic acid, 6-bromohexanoic acid, 5-bromovaleric acid and 4-bromobutyric acid were obtained from Aldrich. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge 60, F_{254}). The intermediates and target molecules prepared were purified following column chromatographic separation techniques using either neutral aluminium oxide or silica gel (100–200 and 230–400 mesh) as a stationary phase. 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) or a Bruker Aveance series DPX-200 (200 MHz) spectrometer and the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on

Scheme



Scheme. Synthetic route employed to prepare the unsymmetric dimers. Reagents and conditions: (i) $AlCl_3/C_3H_7COCl$ or C_4H_9COCl or $C_5H_{11}COCl$ or $C_6H_{13}COCl$, CCl_4; (ii) KOH/N_2H_4, reflux, ethyleneglycol; (iii) 2-methyl-3-butyn-2-ol, $[(C_6H_5)_3P]_2PdCl_2$, Ph_3P, CuI, Et_3N, rt, 12h; (iv) KOH, toluene, 110°C, 2 h; (v) trimethylsilylacetylene, $[(C_6H_5)_3P]_2PdCl_2$, Ph_3P, CuI, Et_3N, rt, 24h; (vi) $Bu_4N^+F^-$, THF, rt, 3h; (vii) $[(C_6H_5)_3P]_2PdCl_2$, Ph_3P, CuI, Et_3N, rt, 24h.

a Jeol JMS-600H spectrometer in FAB^+ mode using 3-nitrobenzylalcohol as a liquid matrix. The elemental analysis was performed using a Perkin-Elmer instrument. The identification of the mesophases and the transition temperatures of the dimers were determined using a polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90). the phase transition enthalpies were measured using a differential scanning calorimeter (Perkin Elmer DSC7).

2.3. *General procedure for the preparation of cholesteryl ω-[4-(4-n-alkylphenylethynyl)phenoxy]alkanoates*

Route A: A mixture of cholesteryl (4-iodophenoxy) alkanoate (**3a–d**) (0.73 mmol), phenylacetylene **4a–d** (0.93 mmol), bis(triphenylphosphine)palladium(II) chloride (20 mg, 0.028 mmol), triphenylphosphine (37 mg, 0.14 mmol), copper(I) iodide (23 mg, 0.12 mmol), THF (10 ml) and triethylamine (10 ml) was heated at 75°C under argon for 16 h. The reaction mixture was filtered while hot through a celite bed. The filtrate was evaporated under vacuum and the pale yellow solid obtained was dissolved in $CHCl_3$ (20 ml) and the resultant solution washed with a 0.2M aqueous HCl (10×2 ml), 5% aqueous NaOH (10×2 ml), water (10×2 ml), brine and then was dried over anhydrous Na_2SO_4. Evaporation of the solvent furnished a pale yellow solid, which was purified by column chromatography using alumina (neutral). Elution with a mixture of 10% EtOAc/hexanes furnished a white solid (60–80% yield) that was further purified by repeated recrystallization with a mixture of CH_2Cl_2/EtOH (1/10) until a constant and sharp isotropic phase transition was obtained.

Route B: A mixture of cholesteryl (4-ethynylphenoxy)-alkanoate (**1a–d**) (0.73 mmol), 4-*n*-alkylbromobenzene **6a–d** (0.93 mmol), bis(triphenylphosphine)palladium(II) chloride (20 mg, 0.028 mmol), triphenylphosphine (37 mg, 0.14 mmol), copper(I) iodide (23 mg, 0.12 mmol), THF (10 ml) and triethylamine (10 ml) was heated at 75°C under argon for 16 h. The work-up and purifications were carried out as described in method A. Characterization details are given below for a representative selection of the final products.

2.3.1. *Cholesteryl 4-[4-(4-n-butylphenylethynyl)-phenoxy]butanoate (**DTA-3,4**)*

This dimer was prepared by both routes A and B; white solid $R_f = 0.42$ (10% EtOAc/hexanes); yield: route A 75%, route B 72%. IR (KBr pellet): ν_{max}, 2931, 1727, 1604, 1518 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.42 (t, $J = 8.84$ Hz, 4H, Ar), 7.14 (d, $J = 8.0$ Hz, 2H, Ar), 6.84 (d, $J = 8.8$ Hz, 2H, Ar), 5.37 (brd, $J = 4.0$ Hz, 1H, $1 \times$ olefinic), 4.6(m, 1H, $1 \times$ CHOCO), 4.0 (t, $J = 6.1$ Hz, 2H, $1 \times OCH_2$), 2.61 (t, $J = 7.7$ Hz, 2H, Ar–CH_2), 2.5–2.3 (m, 4H, $2 \times$ allylic methylene), 2.14–0.95 (m, 35H, $1 \times CH_3$, $13 \times CH_2$, $6 \times CH$), 1.01 (s, 3H, $1 \times CH_3$), 0.91 (d, $J = 6.0$ Hz, 3H, $1 \times CH_3$), 0.87 (d, $J = 1.7$ Hz, 3H, $1 \times CH_3$), 0.85 (d, $J = 1.6$ Hz, 3H, $1 \times CH_3$), 0.67 (s, 3H, $1 \times CH_3$). ^{13}C NMR (100 MHz, CDCl3): 172.5, 158.86, 143.03, 139.71, 133.01, 131.40, 128.44, 122.71, 120.84, 115.83, 114.61, 88.74, 88.32, 74.17, 66.96, 56.78, 56.27, 50.15, 42.40, 39.83, 39.59, 38.22, 37.07, 36.67, 36.27, 35.84, 35.61, 33.40, 31.96, 31.16, 28.26, 28.05, 27.87, 24.75, 24.33, 23.91, 22.83, 22.59, 22.33, 21.11, 19.34, 18.78, 13.92, 11.90. Elemental analysis: calcd (found), C 83.47 (83.03), H 9.72 (9.90)%. FAB Mass $[M]^+$: 704, calculated for $C_{49}H_{68}O_3$.

2.3.2. *Cholesteryl 5-[4-(4-n-pentylphenylethynyl)-phenoxy]pentanoate (**DTA-4,5**)*

This compound was prepared by both routes A and B; white solid $R_f = 0.44$ (10% EtOAc/hexanes); yield: route A 70%, route B 72%. IR (KBr pellet): ν_{max} 2935, 1738, 1602, 1519 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.42 (t, $J = 9.1$ Hz, 4H, Ar), 7.14 (d, $J = 8.3$ Hz, 2H, Ar), 6.84 (d, $J = 8.9$ Hz, 2H, Ar), 5.36 (brd, $J = 4.8$ Hz, 1H, $1 \times$ olefinic), 4.60(m, 1H, $1 \times$ CHOCO), 3.98 (t, $J = 6.52$ Hz, 2H, $1 \times OCH_2$), 2.60 (t, $J = 7.6$ Hz, 2H, Ar–CH_2), 2.38–2.29 (m, 4H, $2 \times$ allylic methylene), 2.05–0.95 (m, 39H, $1 \times CH_3$, $15 \times CH_2$, $6 \times CH$), 1.01 (s, 3H, $1 \times CH_3$), 0.89 (d, $J = 1.36$ Hz, 3H, $1 \times CH_3$), 0.87 (d, $J = 1.8$ Hz, 3H, $1 \times CH_3$), 0.85 (d, $J = 1.8$ Hz, 3H, $1 \times CH_3$), 0.66 (s, 3H, $1 \times CH_3$). Elemental analysis: calcd (found), C 83.55 (83.45), H 9.90 (10.16)%. FAB Mass $[M]^+$: 732, calculated for $C_{51}H_{72}O_3$

2.3.3. *Cholesteryl 6-[4-(4-n-hexylphenylethynyl)-phenoxy]hexanoate (**DTA-5,6**)*

This compound was prepared by both the routes; white solid $R_f = 0.40$ (10% EtOAc/hexanes); yield: route A 76%, route B 78%, IR (KBr pellet): ν_{max} 2947, 1732, 1602, 1517 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.42 (t, $J = 8.2$ Hz, 4H, Ar), 7.14 (d, $J = 8.0$ Hz, 2H, Ar), 6.84 (d, $J = 8.72$ Hz, 2H, Ar), 5.37 (brd, $J = 3.0$ Hz, 1H, $1 \times$ olefinic), 4.63 (m, 1H, $1 \times$ CHOCO), 3.96 (t, $J = 6.36$ Hz, 2H, $1 \times OCH_2$), 2.60 (t, $J = 7.68$ Hz, 2H, Ar–CH_2), 2.31 (m, 4H, $2 \times$ allylic methylene), 2.01–0.93 (m, 43 H, $1 \times CH_3$, $17 \times CH_2$, $6 \times CH$), 1.01 (s, 3H, $1 \times CH_3$), 0.91 (d, $J = 6.56$ Hz, 3H, $1 \times CH_3$), 0.87 (d, $J = 1.72$ Hz, 3H, $1 \times CH_3$), 0.85 (d, $J = 1.72$ Hz, 3H, $1 \times CH_3$), 0.66 (s, 3H, $1 \times CH_3$). ^{13}C NMR (100 MHz, CDCl3): 173.03, 159.03, 143.07, 139.74, 133.00, 131.40, 128.45, 122.68, 120.83, 115.57, 114.56, 88.80, 88.24, 73.89, 67.76, 56.77, 56.23, 50.12, 42.38, 39.81, 39.58,

38.23, 37.06, 36.66, 36.26, 35.94, 35.85, 34.62, 31.95, 31.74, 31.24, 28.94, 28.27, 28.06, 27.89, 25.64, 24.83, 24.34, 23.90, 22.85, 22.61, 21.10, 19.36, 18.78, 14.10, 11.90. Elemental analysis: calcd (found), C 83.63 (83.96), H 10.06 (10.24)%. FAB Mass $[M]^+$: 760, calculated for $C_{53}H_{76}O_3$.

2.3.4. *Cholesteryl 8-[4-(4-n-heptylphenylethynyl)-phenoxy]octanoate (DTA-7,7)*

This compound was prepared by both routes A and B; white solid $R_f = 0.44$ (10% EtOAc/hexanes); yield: 68% (same for both routes), IR (KBr pellet): ν_{max} 2933, 1735, 1610, 1516 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.42 (t, $J = 9$ Hz, 4H, Ar), 7.14 (d, $J = 7.8$ Hz, 2H, Ar), 6.85 (d, $J = 8.6$ Hz, 2H, Ar), 5.37 (brd, $J = 4.2$ Hz, 1H, $1 \times$ olefinic), 4.6 (m, 1H, $1 \times$ CHOCO), 3.98 (m, 2H, $1 \times OCH_2$), 2.59 (t, $J = 7.7$ Hz, 2H, Ar–CH_2), 2.34 (m, 4H, $2 \times$ allylic methylene), 1.98–0.91 (m, 43H, $1 \times CH_3$, $17 \times CH_2$, $6 \times$ CH), 1.01 (s, 3H, $1 \times CH_3$), 0.91 (d, $J = 6.52$ Hz, 3H, $1 \times CH_3$), 0.87 (d, $J = 1.9$ Hz, 3H, $1 \times CH_3$), 0.85 (d, $J = 1.84$ Hz, 3H, $1 \times CH_3$), 0.66 (s, 3H, $1 \times CH_3$). Elemental analysis: calcd (found), C 83.74 (83.68); H 10.29 (10.59)%. FAB Mass $[M]^+$: 802, calculated for $C_{56}H_{82}O_3$.

3. Results and discussion

3.1. *Molecular structural characterization*

The molecular structures of the unsymmetric dimers were confirmed using spectroscopic and elemental analyses. As expected, the IR and ^1H spectra of all the unsymmetric dimers appear similar. The IR spectra show absorption bands in the regions ν_{max}/cm^{-1} 2930–2947, 1716–1743, 1601–1608 and 1515–1519 due to C–H (paraffinic), carbonyl (C–O of ester), C–C (aromatic and oleficnic) stretching vibrations, respectively. In the ^1H NMR spectrum, eight aromatic protons appear in the form of three patterns namely, a triplet (t), a doublet (d), and a d in the region of δ 7.4–7.42, 7.1–7.14, and 6.84–6.85, respectively. The olefinic proton, the methine proton adjacent to the ester, the oxymethylene proton in the paraffinic chain, and methylene protons attached to a phenyl ring resonate in the regions δ 5.36–5.37, 4.6–4.63, 3.95–4.02 and 2.59–2.6 as a broad d, multiplet (m), t and t, respectively. The spectral pattern in the region $\delta = 0$–2 appears very complex, but the protons of five methyl groups of the cholesterol moiety can be identified. The *gem*-dimethyl protons appear as two doublets, resonating sharply at $\delta = 0.85$ and 0.87 in all cases. The protons of the two methyl groups attached to quaternary carbon centres appear as two singlets in the regions $\delta = 0.99$–1.01 and 0.66–0.67. The protons of the methyl group attached to a methine carbon appear as a d in the region $\delta = 0.89$–0.91. The ^{13}C NMR spectra have been recorded and listed for **DTA-3,4** and **DTA-5,6** as representative cases. As expected the ^{13}C NMR spectra for both the compounds show 13 signals at higher frequencies. We discuss the ^{13}C NMR spectrum for the compound **DTA-3,4:** the C–O carbon resonates at $\delta = 172.5$ whereas 10 sp^2-hybridized carbons resonate at about $\delta = 158.9$, 143, 139.7, 133, 131.4, 128.4, 122.7, 120.8, 115.8 and 114.6. The signals due to two sp-hybridized carbons appear at $\delta = 88.7$ and 88.3. The signals of other carbons appearing at lower frequency are found to be consistent with the proposed structure (see experimental section for details).

3.2. *Evaluation of mesomorphic behaviour*

The thermal behaviour of the unsymmetric dimers synthesized was examined under an optical polarizing microscope using either clean untreated glass slides or slides treated for homogeneous or for homeotropic alignment of the molecules. The phase transition temperatures and associated enthalpy changes were determined using differential scanning calorimetry. Figures 1 (a) and 1 (b) show the DSC thermograms of the first heating and cooling cycles for the dimers, respectively. The table summarizes the thermal behaviour of all the dimers. The first set of dimers having a C_3-alkylene spacer, in general exhibit enantiotropic SmA, TGB and N* phases. The presence of the N* phase was confirmed by the observation of a characteristic oily streak texture which on slight shear changed to a planar texture when the sample was on an ordinary glass plate. The SmA phase was confirmed by the microscopic observation of a characteristic focal-conic texture for slides treated for planar orientation and a dark field of view for slides treated for homeotropic orientation. Figure 2 shows a typical focal-conic texture of the SmA phase seen at 178°C for **DTA-3,5** during cooling. The TGB phase was identified by the observation of a filament texture on heating from a homeotropic SmA phase. The existence of a TGB phase over a narrow thermal range was confirmed by the simultaneous appearance of textures corresponding to SmA, a TGB and N* for a short period. Figure 3 shows a photomicrograph of the texture observed for **DTA-3,5** on heating from the homeotropic SmA phase in which the textures corresponding to SmA, TGB and N* can be seen. **DTA-3,5** and **DTA-3,6** show a monotropic chiral smectic (SmC*) phase in addition, that was assigned by the observation of dechiralization lines on top of the focal-conic texture with slides treated for planar orientation, while a cloudy texture appeared using slides treated for homeotropic alignment. The planar texture of the SmC* phase seen at room temperature for **DTA-3,5** is shown

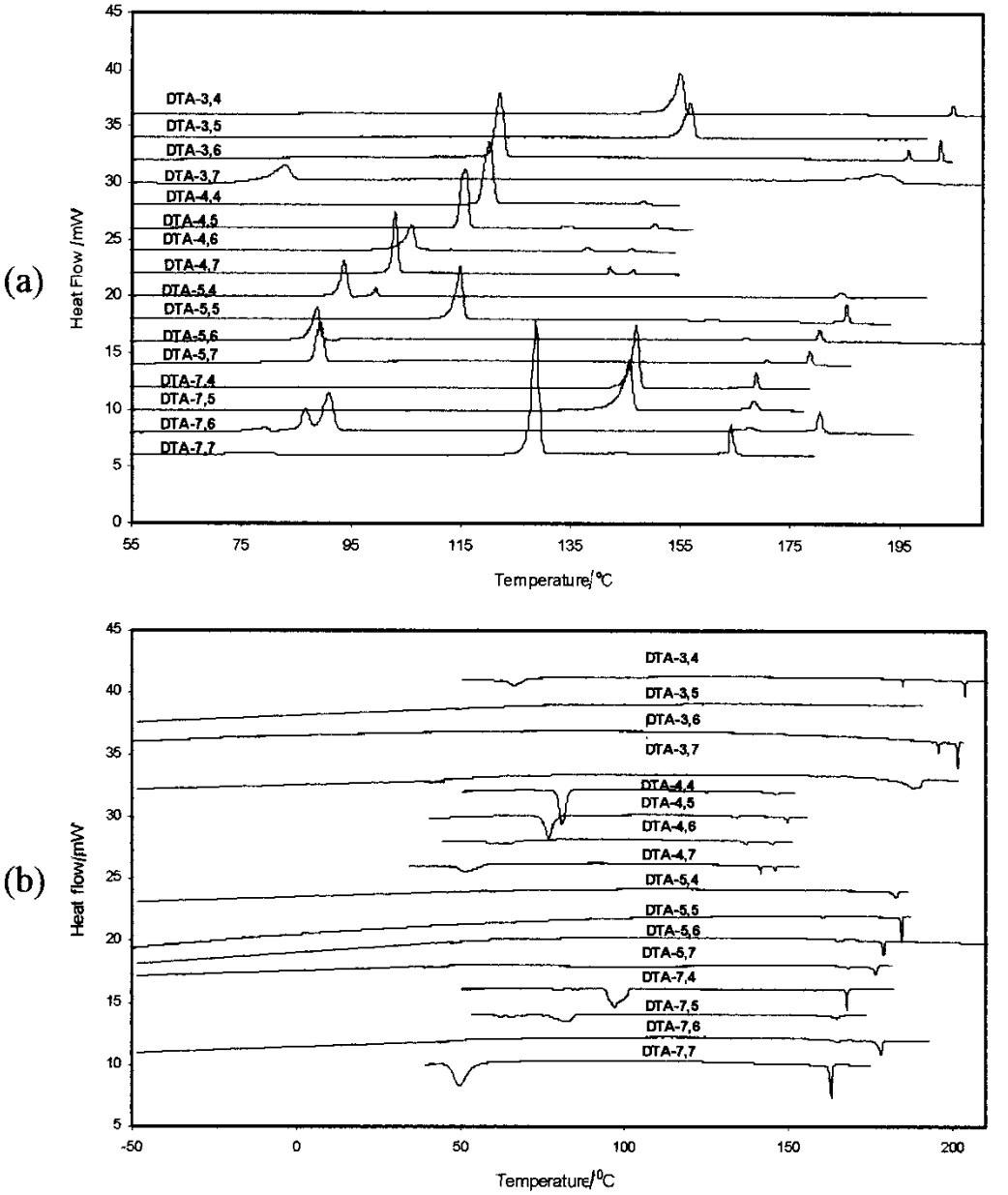


Figure 1. DSC thermograms (*a*) of the first heating cycle and (*b*) of the first cooling cycle of all the dimers.

in figure 4. Interestingly, in both compounds the SmC* phase supercools to -60°C, the lowest temperature that could be achieved using the instrument. However on subsequent heating the samples crystallize.

Compounds **DTA-4,4**, **DTA-4,5**, **DTA-4,6** and **DTA-4,7**, containing a C_4 spacer show enantiotropic SmA, TGB and N* phases. These dimers also show a transient blue phase with the exception of **DTA-4,6**. The texture of the blue phase observed on cooling from the isotropic phase for **DTA-4,5** is shown in figure 5. As can be seen, in the table of all the compounds reported here, these dimers show the lowest clearing temperatures. The same is also true for the Cr–SmA, SmA–TGB–N* transition temperatures. The significant differences in transition temperatures, especially in the clearing temperatures, can be explained as follows. In these compounds, the cholesterol moiety and the tolane core are linked to the alkylene spacer via a carbonyl group and an ether linkage, respectively. In these and similar types of compounds (dimers), the conventional way of accounting for the parity of the spacer is to consider only the number of methylene units (as in this presentation). For example **DTA-3,*R*, DTA-5,*R*** and **DTA-7,*R*** are considered to be odd-members because

Table 1. Transition temperatures (°C)[a] and enthalpies (J g^{-1}) of the cholesteryl ω-[4-(4-*n*-alkylphenylethynyl)phenoxy]alkanoates; the enthalpy values are enclosed in brackets. I = isotropic liquid; BP = blue phase; N* = chiral nematic phase; TGB = twist grain boundary phase; SmA = smectic A phase; SmC* = chiral smectic C phase; Cr = Crystal.

Dimer	*n*	*R*	Cr	Heating Cooling	SmC*	Heating[c] Cooling	SmA	Heating Cooling	TGB	Heating Cooling	N*	Heating Cooling	BP	I
DTA-3,4	3	C_4H_9	•	155.0 (46.1) 66.5 (16.4)	—		•	186.8 (1.5) 184.8 (1.2)	•	[b]	•	204.7 (6) 203.8 (5.8)	—	•
DTA-3,5	3	C_5H_{11}	•	153.6 (37.4)	•	— 81.7[e]	•	178.1 (0.8) 175.3 (0.7)	•	[b]	•	195.6 (4.6) 194.2 (4.2)	—	•
DTA-3,6	3	C_6H_{13}	•	119.3 (42.4)	•	— 81.9[e]	•	196.4 (1.1) 195.7 (0.9)	•	[b]	•	202.4 (5.4) 201.5 (5.1)	—	•
DTA-3,7	3	C_7H_{15}	•	82.8 (84)	—		•	193.3[c] 192.3[c, e]	•	[b]	•	196.3 (7.5) 194.6 (6.5)	—	•
DTA-4,4	4	C_4H_9	•	118.2 (40.7) 80.9 (18.4)	—	—	•	126.8 (0.8) 125.0 (0.8)	•	[b]	•	148.3 (1.2) 146.0 (1.1)[d]	•	•
DTA-4,5	4	C_5H_{11}	•	115.8 (34.5) 76.7 (20.3)	—	—	•	134.6 (0.7) 134.0 (0.6)	•	[b]	•	150.4 (1.1) 149.6 (1)[d]	•	•
DTA-4,6	4	C_6H_{13}	•	105.9 (27.5) 63.0 (9.3)	—		•	138.1 (1.3) 137.1 (1.2)	•	[b]	•	146.1 (1.1) 145.3 (1)	—	•
DTA-4,7	4	C_7H_{15}	•	103.0 (48.2) 51.6 (22.6)	—	—	•	142.2 (2.0) 141.5 (2)	•	[b]	•	146.5 (1.2) 146 (1.1)[d]	•	•
DTA-5,4	5	C_4H_9	•	99.5[f] (3.5)	•	— 83.4[e]	•	152.5 (1) 151.5 (0.8)	•	[b]	•	186.1 (5.1) 184.8 (4.7)	—	•
DTA-5,5	5	C_5H_{11}	•	114.9 (35.7)	•	— 84.2[e]	•	161.4 (0.5) 160.4 (0.5)	•	[b]	•	185.4 (5.3) 184.4 (4.6)	—	•
DTA-5,6	5	C_6H_{13}	•	88.8 (30.5)	•	100.4 98.9[e]	•	166.7 (1) 165.5 (1)	•	[b]	•	180.3 (5) 178.9 (4.7)	—	•
DTA-5,7	5	C_7H_{15}	•	108.0 (34.5)	•	— 99.7[e]	•	170.8 (1.5) 167.8 (1.3)	•	[b]	•	178.7 (5.2) 176.4 (5.0)	—	•
DTA-7,4	7	C_4H_9	•	146.9 (58.1) 97.0 (37)	—		•	— 132.6 (0.3)	•	[b]	•	168.8 (5) 167.8 (4.7)	—	•
DTA-7,5	7	C_5H_{11}	•	145.7 (56.9) 82.3 (16.4)	—		—		—	[b]	•	168.4 (4.6) 164.6 (4.2)	—	•
DTA-7,6	7	C_6H_{13}	•	90.9[f] (16.7)	•	97.9 95.9[e]	•	167.5 (1.1) 165.0 (1.1)	•	[b]	•	180.3 (5.2) 178.3 (4.8)	—	•
DTA-7,7	7	C_7H_{15}	•	128.3 (47.4) 49.7 (19)	•	— 93.3	•	139.8[c] 138.7[c]	•	142.4[e] 141.3[e]	•	164.1 (6.1) 162.9 (5.8)	—	•

[a]Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at 5°C min^{-1}.
[b]TGB is a transient phase and it can have either SmA or SmC blocks.
[c]The phase transition was observed under polarizing microscope and was too weak to be seen in DSC.
[d]The I–N* transition passes through a transient BP.
[e]The transition from mesophase to crystallization was not observed up to −60.0°C.
[f]An additional crystal to crystal transition was observed for the compounds **DTA-5,4** and **DTA-7,6** at 93.7/31.9 and 86.6/6.5°C respectively.

in these dimers three, five and seven methylene units separate the two rigid cores; whereas if the carbon atom of the carbonyl group is also taken as a part of the central spacer, then these would be even-members. However, for the sake of consistency with the convention followed in the literature and in our earlier publications [5–10], we count only the number of methylene units in considering the parity of the spacer. It is now well documented that in such dimers the two mesogenic segments, connected through an even-parity flexible spacer, are almost antiparallel to each other imparting almost a rod-like shape to the dimer. In the case of an odd-member, the mesogenic segments are inclined with respect to each other and thus the molecular shape is bent. Owing to the reduced anisotropy in the bent molecules the transition temperatures are obviously much lower when compared with the dimers having a linear conformation. This could be the reason for DTA-3,*R*, DTA-5,*R* and **DTA-7,*R*** (in which the total number of carbons in the spacer are 4, 6 and 8, respectively) exhibiting higher clearing temperatures than **DTA-4,*R*** (in which the spacer is C_5).

The dimers containing a C_5 spacer (**DTA-5,4**, **DTA-5,5**, **DTA-5,6** and **DTA-5,7**) show enantiotropic SmA, TGB and N* mesophases. In addition these compounds exhibit a monotropic SmC* phase with the exception of **DTA-5,6** in which it is enantiotropic. Interestingly in all these cases the SmC* phase supercools to −60°C. It

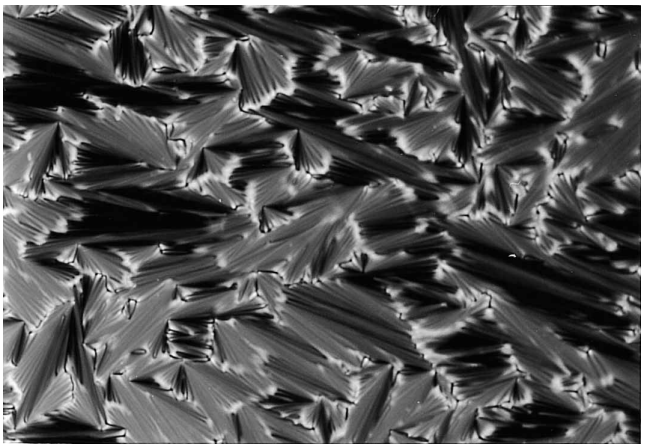


Figure 2. Photomicrograph of the characteristic focal-conic texture of the SmA phase observed at 178°C for **DTA-3,5** during cooling.

may be mentioned here that Cha *et al*. have also reported the synthesis and characterization of **DTA-5,4** [5*e*] and this was denoted **KI-5T**. The mesopmorphic behaviour of **DTA-5,4** agrees with **KI-5T** with the exception that **DTA-5,4** shows a monotropic SmC* phase. The compounds containing the next highest spacer length (C_7) namely **DTA-7,4**, **DTA-7,5**, **DTA-7,6** and **DTA-7,7** exhibit an enantiotropic N* phase. In addition **DTA-7,4** shows a monotropic SmA and a transient TGB phase, whereas these phases are enantiotropic for **DTA-7,6**. The latter compound also shows a monotropic SmC* phase which again supercools to −60°C. **DTA-7,7** exhibits enatiotropic SmA and TGB phases in addition to a SmC* phase that occurs till 50°C. In general however it can be seen that increasing

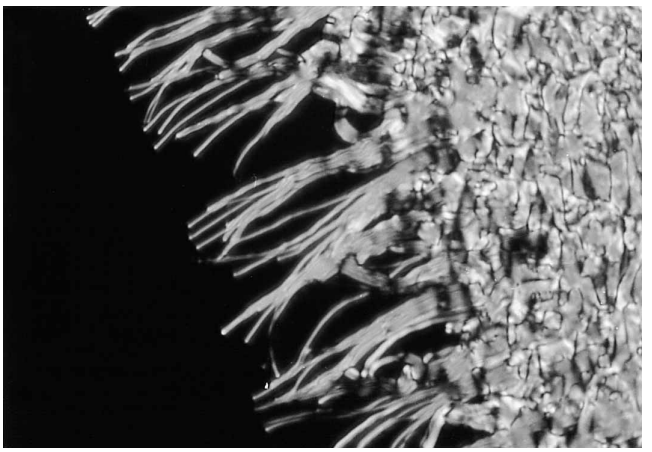


Figure 3. Photomicrograph of the texture observed for **DTA-3,5** on heating from the homeotropic SmA phase. Note the textures corresponding to SmA (left portion; dark field of view), TGB (middle portion: filaments) and N* (right portion: non-specific, but on shear gives planar texture) appearing simultaneously for a short period.

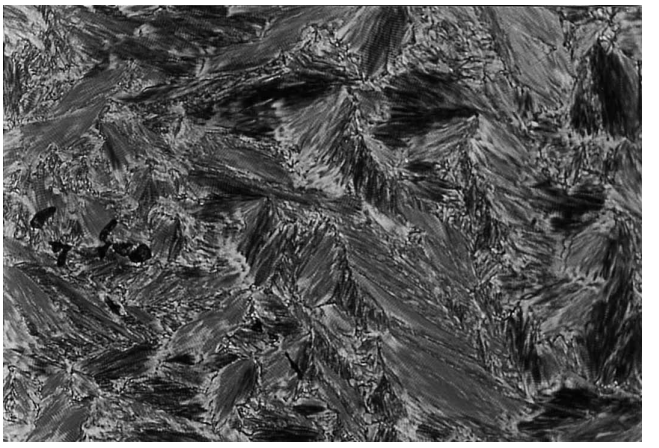


Figure 4. Photomicrograph of the texture of SmC* seen for **DTA-3,5** at room temperature (about 30°C). Note the broken focal-conic texture with dechiralization lines.

the spacer length increases the thermal range of the N* phase whereas increasing the length of the alkyl tail enhances the stability of smectic phases.

4. Summary

We have reported the synthesis and characterization of a new series of unsymmetric dimers consisting of a diphenylacetylene moiety having an alkyl chain and a cholesteryl ester unit linked through a parafinic spacer. The lengths of both the methylene spacer and the alkyl chain have been varied. In general, all the dimers exhibit an enantiotropic chiral nematic phase. The first set of dimers containing a C_3 spacer exhibit smectic A, twist grain boundary and chiral nematic phases, while the dimers with *n*-pentyl and *n*-hexyl chains also show a monotropic chiral smectic phase. The dimers containing a C_4 spacer show SmA, TGB, N* and blue phases except for the *n*-hexyl homologue, which does not show

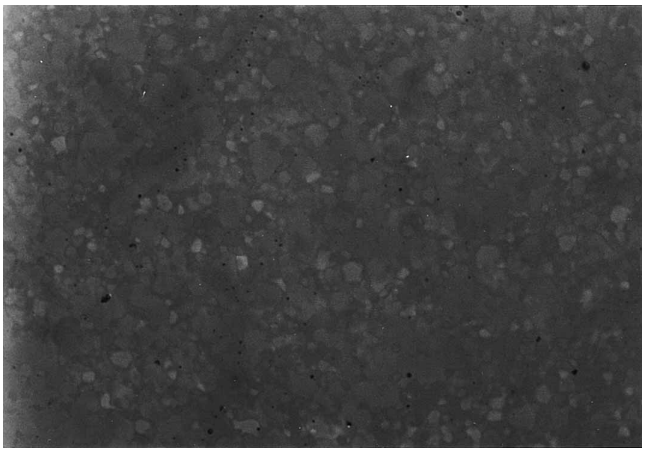


Figure 5. Photomicrograph of the texture of the blue phase observed on cooling **DTA-4,5** from the isotropic phase.

a BP phase. Among the four compounds having a C_5 spacer, the dimer with an *n*-hexyl tail exhibits enantiotropic SmC* SmA, TGB and N* phases while the others show the same behaviour except that the SmC* phase is monotropic. Interestingly, in all these compounds the SmC* phase supercools to -60°C. In a set of compounds having a C_7 spacer, the dimer with an *n*-pentyl chain shows only a N* phase while the *n*-butyl homologue also shows SmA and TGB phases. The *n*-hexyl homologue shows SmC*, SmA, TGB and N* phases. The *n*-heptyl homologue shows similar behaviour, with the exception that the SmC* phase is monotropic. In these compounds the length of the central spacer appears to have some effect on mesomorphic behaviour, while the variation in length of the alkyl terminal chain has a weak effect on the phase transition temperatures.

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