Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Published online: 20 Oct 2010.

To cite this article: K. C. Majumdar , S. Ponra & S. Chakravorty (2010): Synthesis and Characterization of Cholesterol-Based Tetramers, Molecular Crystals and Liquid Crystals, 528:1, 113-119

To link to this article: http://dx.doi.org/10.1080/15421406.2010.504628

Mol. Cryst. Liq. Cryst., Vol. 528: pp. 113–119, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.504628

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Synthesis and Characterization of Cholesterol-Based Tetramers

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Novel symmetrical liquid-crystal tetramers were designed and synthesized. The length of the central spacer and the outer spacers has been varied. The molecular structures of the target compounds were confirmed by Fourier transform infrared and proton nuclear magnetic resonance spectroscopy. The thermal phase behavior of the tetramers was investigated by polarizing optical microscopy and differential scanning calorimetry. All of the liquid-crystal tetramers showed either a chiral nematic mesophase or chiral nematic and smectic mesophases.

Keywords Chiral nematic phase; cholesterol-based tetramer; DSC; POM; smectic phase

Introduction

Since the discovery of the liquid-crystal dimers [1] and subsequent interest in these materials [2], many dimeric systems have been reported. Liquid-crystal dimers are of interest because they can act as models for main group liquid-crystalline polymers that allow the study of the flexibility and properties of different mesogenic compounds. Thus, dimeric liquid crystals retain the crucial structural components of many thermotropic main group polymers, namely, a flexible spacer linking two mesogenic groups, yet they are easier to study and are amenable to a more straightforward interpretation. Furthermore, as a distinct class of compounds with unusual properties and potential for application, dimeric liquid crystals are of interest in their own right. There are remarkable differences in the meosphase behaviors of nonsymmetric and symmetric dimers. Nonsymmetric liquid-crystal dimers usually exhibit an intercalated smectic phase, in which specific molecular interactions between the two different meosgenic units account for this specific behavior [3–5]. In contrast, symmetric liquid-crystal dimers exhibit monolayer smectic phases [6]. In general, mesophase behavior of liquid-crystal dimers depends on several factors, such as the structure and size of the mesogenic units, the chemical structure, and the length of the spacers and terminal groups [7–10]. Due to the fact that cholesterol is abundant in nature and a commercially available chiral compound, liquid-crystal dimers

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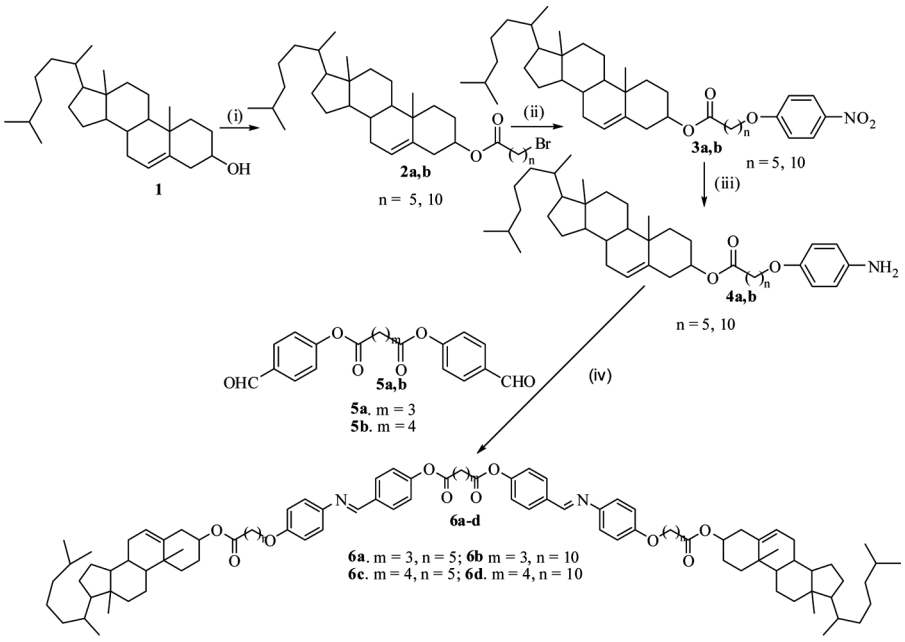
possessing a cholesteryl ester unit joined to different aromatic mesogens through an alkyne spacer are currently receiving considerable interest as chiral dimers [11–15]. The main interest behind the design of new materials containing cholesteryl groups results from its rigid, long shape and chiral structure. A rigid, long shape induces large intramolecular interaction via Van der Waals forces stabilizing parallel molecular arrangements and the chiral structure induces chirality in molecular order; that is, a helical superstructure. A liquid-crystal trimer consists of molecules containing three mesogenic units interconnected via two flexible spacers. These structural components may be assembled in a number of ways to give, for example, linear trimers [16,17], trimers in which one or more mesogenic units are connected in a lateral position [18,19], cyclic trimers [20–21], star-shaped trimers [22,23], and trimers containing rod-like and disc-like mesogenic moieties [24,25]. On the other hand, liquid-crystal tetramers consist of molecules containing four interconnected mesogenic units linked via three flexible spacers.

In continuation of our effort to synthesize different cholesterol-based liquid-crystalline compounds [26–29] we present a series of cholesterol-based liquid-crystalline tetramers that look like a combination of two nonsymmetric dimers separated by a flexible central spacer. We have varied the length of the central mesogenic units as well as the spacer length of the two unsymmetrical dimeric counterparts.

The reaction between cholesterol and *n*-bromohexanoyl chloride in tetrahydrofuran (THF) at room temperature gave the corresponding ester derivatives **2a,b**. The ester derivatives were then subjected to alkylation with *p*-nitrophenol in refluxing acetone in the presence of anhydrous potassium carbonate to afford the desired nitro derivatives **3a,b**. The nitro derivatives **3a,b** on hydrogenation afforded the



Scheme 1. Reagents and reaction conditions: (i) THF, pyridine, bromo-alkanoylchloride rt, 12 h, (ii) p-nitrophenol, acetone, reflux, 16 h; (iii) Pd/C, H_2, EtOAc (solvent); (iv) EtOH, glacial AcOH, reflux.

corresponding amine derivatives **4a,b**. The aldehydes **5a,b** and amines **4a,b** derivatives on condensation afforded a series of compounds **6a-d** (Scheme 1).

Experimental

General Procedure for the Preparation of Compounds 5a,b

Compounds **5a,b** were prepared according to the literature procedure [30].

General Procedure for the Preparation of Compounds 2, 3, and 4

All compounds were prepared according to the published procedure [26].

General Procedure for the Preparation of Compounds 6a-d

Compound **5a** (0.1 g, 0.03 mmol) was heated under reflux with the amine derivative **4a** (0.38 g, 0.06 mmol) in absolute ethanol (10 mL) in the presence of a catalytic amount of glacial acetic acid to afford the desired product **6a**. All other compounds were prepared similarly.

*Compound **6a***. Yield 92%, white solid. IR (KBr) ν_{max}: 2932, 1760, 1738, 1625, 1603 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): $\delta_H = 8.46$ (s, 2H), 7.90 (d, 4H, $J = 8.6$ Hz), 7.20–7.22 (m, 8H), 6.90 (d, 4H, $J = 8.8$ Hz), 5.36 (d, 2H, $J = 4.0$ Hz), 4.61–4.63 (m, 2H), 3.96 (t, 4H, $J = 6.5$ Hz), 2.75 (t, 4H, $J = 7.2$ Hz), 2.30 (t, 8H, $J = 7.5$ Hz), 0.67–2.24 (m, 96H). Molecular formula: $C_{97}H_{134}N_2O_{10}$, CHN calculated, C, 78.29; H, 9.08; N, 1.88%; found, C, 78.50; H, 8.82; N, 1.97%.

*Compound **6b***. Yield 95%, white solid. IR (KBr) ν_{max}: 2932, 1760, 1738, 1625, 1603 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): $\delta_H = 8.46$ (s, 2H), 7.90 (d, 4H, $J = 8.6$ Hz), 7.20–7.21 (m, 8H), 6.90 (d, 4H, $J = 8.6$ Hz), 5.36 (d, 2H, $J = 4.0$ Hz), 4.57–4.64 (m, 2H), 3.95 (t, 4H, $J = 7.2$ Hz), 2.75 (t, 4H, $J = 7.2$ Hz), 0.67–2.31 (m, 124H). ^{13}C-NMR ($CDCI_3$, 100 MHz): 173.3, 171.0, 158.0, 156.9, 152.6, 144.5, 139.7, 134.3, 129.7, 122.6, 122.2, 121.9, 115.0, 73.7, 68.3, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 34.7, 33.2, 31.9, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.2, 28.0, 27.8, 26.0, 25.0, 24.3, 23.8, 22.8, 22.6, 21.0, 19.9, 19.3, 18.7, 11.9. Molecular formula: $C_{107}H_{154}N_2O_{10}$, CHN calculated, C, 78.92; H, 9.53; N, 1.72%; found, C, 79.10; H, 9.58; N, 1.94%.

*Compound **6c***. Yield 86%, white solid. IR (KBr) ν_{max}: 2944, 1743, 1623, 1603, 1578 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz): $\delta_H = 8.46$ (s, 2H), 7.89 (d, 4H, $J = 8.6$ Hz), 7.20–7.21 (m, 8H), 6.89–6.93 (m, 4H), 5.36 (d, 2H, $J = 4.0$ Hz), 4.58–4.66 (m, 2H), 3.96 (t, 4H, $J = 6.4$ Hz), 2.67 (t, 4H, $J = 7.2$ Hz), 2.30 (t, 8H, $J = 7.6$ Hz), 0.67–1.98 (m, 98H). Molecular formula: $C_{98}H_{136}N_2O_{10}$, CHN calculated, C, 78.36; H, 9.13; N, 1.86%; found, C, 78.10; H, 9.41; N, 1.97%.

*Compound **6d***. Yield 85%, white solid. IR (KBr) ν_{max}: 2935, 1752, 1736, 1622, 1604 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): $\delta_H = 8.45$ (s, 2H), 7.89 (d, 4H, $J = 8.6$ Hz), 7.20 (d, 4H, $J = 8.8$ Hz), 7.17 (d, 4H, $J = 8.6$ Hz), 6.90 (d, 4H, $J = 8.6$ Hz), 5.37 (d, 2H, $J = 4.1$ Hz), 4.61–4.66 (m, 2H), 3.95 (d, 4H, $J = 6.5$ Hz), 2.59 (t, 4H, $J = 7.2$ Hz), 0.67–2.35 (m, 126H). Molecular formula: $C_{108}H_{156}N_2O_{10}$, CHN calculated, C, 78.98; H, 9.57; N, 1.71%; found, C, 79.19; H, 9.73; N, 1.78%.

Results and Discussion

The phase transition temperatures were determined using differential scanning calorimetry. Table 1 shows the phase sequence, transition temperatures, and associated enthalpies of the tetramers.

All the tetramers exhibit simple thermal behavior. All the tetramers **6a-d** exhibit enantiotropic phase behavior. The tetramers **6a, 6c, 6d** exhibit only one mesophase in addition to several solid–solid transitions, whereas the tetramer **6b** exhibits two mesophases in addition to one solid–solid phase transition. On cooling from the isotropic phase the tetramers **6a, 6c**, and **6d** exhibit characteristic cholesteric fan textures of the N^* phase [31]. The three compounds also exhibit oily streak textures of the N^* phase in heating cycles. On cooling from the isotropic phase, compound **6b** (compound was placed in a polyamide-coated thin cell of thickness $d = 5 \pm .02\,\mu m$) exhibits a characteristic texture of the N^* phase [31]; on further cooling a phase transition occurs at around 179°C and after that a broken focal conic texture of the SmA phase appears. On further cooling compound **6b** solidifies.

Powder X-ray diffraction was carried out on a Philips powder diffractometer (The Raman Research Institute, Bangalore, India), equipped with a temperature controller permitting low- as well as high-temperature operation as needed (with CuKα radiation of $\lambda = 1.5418\,nm$) to confirm the mesophase structure of compound **6b**. A high-resolution X-ray diffraction (HRXRD) diagram of compound **6b** at 160°C is represented in Fig. 1. The diffraction diagram exhibits a sharp peak in the small angle region with $\theta = 0.693$ ($d = 63.68$ Å) and a broad, diffuse peak in the wide angle region.

The sharp Bragg's reflection in the small angle region is due to one-dimensional layering in the condensed SmA phase and a diffuse peak in the wide angle region is due to liquid-like correlation of the molecules. The calculated molecular length from molecular modeling is about 56.77 Å. So we expected a partial bilayer arrangement within the SmA phase.

Tamaoki *et al.* [32] synthesized dicholesteryl ester of diacetylenedicarboxylic acid with different lengths of methylene linkages. They observed that all the compounds

Table 1. Phase transition temperature (degree) and associated enthalpies (KJ/mol^{-1} in parantheses) in heating cycles of DSC experiment

Compound 6a:

$$Cr \xrightarrow[(1.9)]{161.5} Cr_1 \xrightarrow[(50.6)]{178.6} N^* \xrightarrow[(12.5)]{258.4} I$$

Compound 6b:

$$Cr \xrightarrow[(3.7)]{78.4} Cr_1 \xrightarrow[(17.6)]{152.7} SmA \xrightarrow[(2.6)]{179.2} N^* \xrightarrow[(3.9)]{196.8} Cr$$

Compound 6c:

$$Cr \xrightarrow[(21.8)]{136.6} Cr_1 \xrightarrow[(2.0)]{174.6} Cr_2 \xrightarrow[(43.2)]{178.6} N^* \xrightarrow[(29.4)]{278.9} I$$

Compound 6d:

$$Cr \xrightarrow[(86.0)]{145.3} N^* \xrightarrow[(1.8)]{184.8} I$$

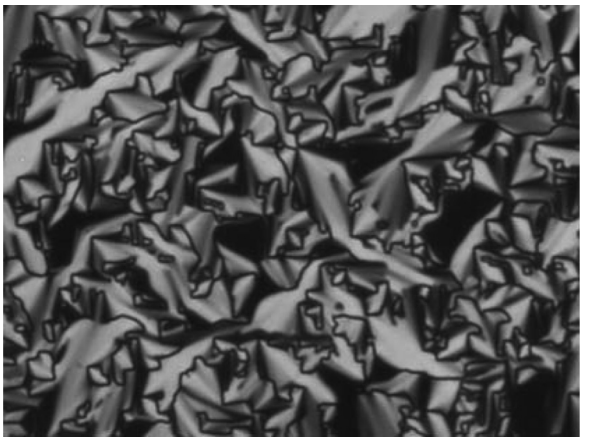


Figure 1. Compound **6b** at 190°C.

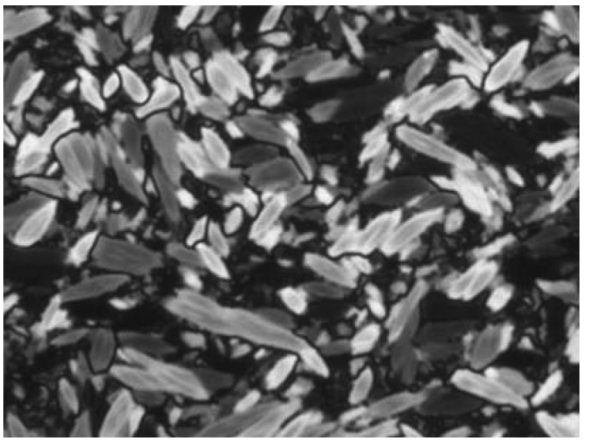


Figure 2. Compound **6b** at 171.9°C.

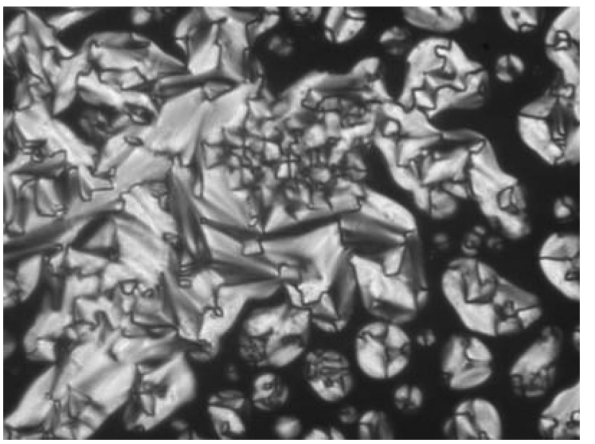


Figure 3. Compound **6c** at 260°C.

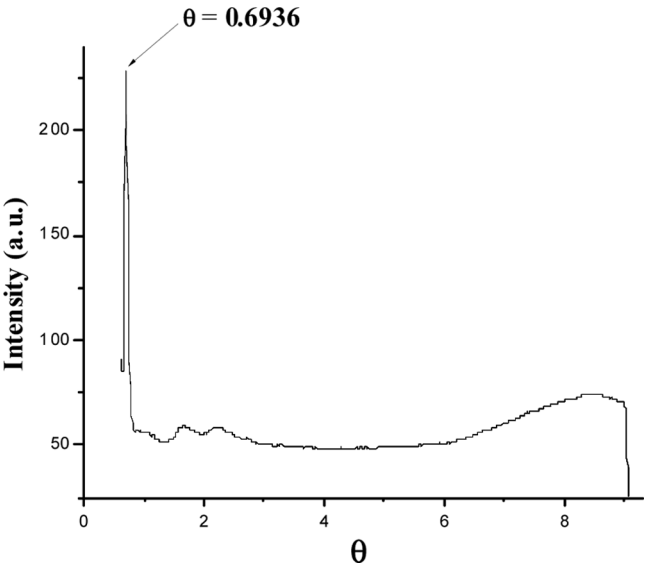


Figure 4. HRXRD diagram of compound **6b** at 160°C.

exhibit a cholesteric phase. Henderson and coworkers [33–35] have synthesized six closely related homologous series of tetramers by varying the length and parity of the flexible spacers and by varying the molecular shape. The tetramers exhibit N^* and SmA and/or N^*, SmA phase behavior. In this article we have mainly focused on the synthesis of cholesterol-based tetramer. All the compounds exhibit mesomorphism. Three of the four tetramers exhibit the N^* phase and one exhibits the N^* phase in addition to the SmA phase.

Acknowledgment

Two of us (S.P. & S.C.) thank the Department of Science and Technology (New Delhi) for financial assistance. We are grateful to the Council of Scientific & Industrial Research (CSIR) (New Delhi) for their fellowships. We are also thankful to Dr. Raghunathan of Raman Research Institute, Bangalore, for providing the HRXRD data.

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