



Synthesis, characterization and molecular organization for induced smectic phase of triazole ring in non-symmetric liquid crystalline dimer



Guan-Yeow Yeap^{a,*}, Arwa Alshargabi^a, Wan Ahmad Kamil Mahmood^a,
Chun-Chieh Han^b, Hong-Cheu Lin^b, Minoru Santo^c, Masato M. Ito^c

^a Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, Minden 11800, Penang, Malaysia

^b Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan, People's Republic of China

^c Faculty of Science & Engineering, Soka University, 1-236 Tangi-cho, Hachioji, Tokyo 192-8577, Japan

ARTICLE INFO

Article history:

Received 2 February 2015

Received in revised form 22 March 2015

Accepted 13 April 2015

Available online 24 April 2015

Keywords:

Dimer

Cholesterol

Click chemistry

Frustrated mesophase

ABSTRACT

New non-symmetric liquid crystal dimers containing cholesterol, triazole and biphenylene segments have been synthesized via click reaction. Increase in the flexible spacers length affects the mesophase formation. The homologues with short and medium alkyl spacer exhibit SmA* and SmC* phases whilst the analogue with the longest spacer favors the formation of enantiotropic SmA and N* phases. The XRD studies reveal the emergence of the SmA* and SmC* phases that can be associated with the monolayer ordering of these dimers. Further investigation through a comparison study shows that the triazole ring affects the mesophase formation wherein apart from the molecular dipole the subtle electrostatic interaction and van der Waal's forces enhance the SmC* phase.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

A dimer is a simplest type of oligomer in which molecules composed of two mesogenic units connected to a flexible spacer. There are two classes of dimers: symmetric and unsymmetric dimers.¹ Chiral liquid crystal dimers, both symmetric and non-symmetric, were discovered more than a decade ago and they continue to receive great attention by researchers even until today.² This is because the chiral LC phases, which formed either by self-assembly or when incorporated in a host of non-chiral LC phase, are classified intrinsically by i) the unique properties such as frustrated and re-entrant mesophases³ and ii) the structures promising both advanced technology and fundamental research.⁴

Frustrated fluid phases such as blue phases (BPs)⁵ and twist grain boundary (TGB) phases⁶ are of special interest as they arise from antagonistic situations in which the molecules organized in a certain manner. The helical structures of chiral nematic (N*) or chiral smectic C (SmC*) and chiral smectic A (SmA*) have been used in thermochromic and electro-optic devices as well as spatial light modulation applications.⁷

Cholesterol is one of the chiral compounds available naturally and commercially. It possesses a rigid aliphatic structure with eight chiral centres, which are essential in inducing liquid crystallinity especially in non-symmetric dimers. Hence, it has been widely used as the chiral liquid crystal group.

Similarly, the biphenyl core has received considerable attention not only because low molar mass substances as well as polymers containing this core are chemically and/or photochemically stable⁸ but some of these systems have revolutionized liquid crystal science in general and display technology in particular.⁹ The phase behavior of the biphenyl dimers containing a chiral moiety can exhibit N* and/or SmA phases¹⁰ and in some cases SmC* and TGB phases are also seen.¹¹

The dimers with ester or ether moieties show odd even effect on the phase transition and the associated entropy changes when the length and parity of the spacer were varied.¹²

Recently, many cholesteryl esters with more complex structures have been designed and synthesized.¹³ Non-symmetric dimers derived from cholesterol, aromatic mesogen and heteroatom core represent an exemplary and emerging class of new chiral liquid crystals.¹⁴ One of the typical groups among these systems can be related to the five-membered ring such as [1,2,3]-triazole formed by [2+3] dipolar cycloaddition reaction between an organic azide and terminal alkyne, also known as 'Click Chemistry',¹⁵ which has

* Corresponding author. Fax: +60 4 6574854; e-mail address: gyyeap@usm.my (G.-Y. Yeap).

attracted great attention in the field of materials chemistry,¹⁶ organic chemistry, supramolecular chemistry,¹⁷ drug discovery and bio-conjugation.¹⁸ One of these materials can be illustrated by the trimer with two cholesterol connected by a triazole core via alkyl spacer, which formed TGB, N* and SmC* phases.¹⁹ Majumdar et al., reported a substituted phenyl oxadiazole unit, which was connected to the cholesterol alkanolate group, which entailed the formation of N*, PB and TGBC* with long thermal stability range phases.²⁰ In addition, bent-shaped molecule containing a cholesterol unit as one of the side arms connected to 1,2,3-triazole ring while the other arm of the triazole ring is connected to two- and three-ring aromatic systems with varying terminal chain lengths have been synthesized. These homologues exhibited SmA*, SmC* and TGBC*.²¹

In the present article we intend to i) synthesize a new architecture dimers, which contain cholesterol, biphenylene and triazole core connected by different flexible spacers in one system; ii) investigate the effect of the variable spacer length on the mesophase formation and iii) study the effect of triazole core in the mesophase formation with a previous work on (S)-2MBbip-*n*-Chol series as reported by Donaldson et al.^{10a}

2. Results and discussion

The target compounds are derived from the CuI-catalyzed cycloaddition between **2** and **4** (Scheme 1). The initial step involves the esterification of cholesterol by using bromoalkanoic acid in the presence of DCC and DMAP, as described by Donaldson et al.,^{13a} to yield **1a–1f**. The azido group was subsequently introduced at the terminal bromo group **1a–1f** by nucleophilic substitution reaction using sodium azide to afford **2a–2f**.

On the other hand, 4-(4-hydroxyphenyl)benzoic acid was reacted with \pm 2-methyl-1-butanol in acidic medium to afford intermediate **3**,²² which was then reacted with propargyl bromide in the presence of potassium hydroxide to afford compound **4** as a pale yellow oil. Finally, the desired triazole cored **5a–5f** were obtained from the click reaction condition wherein compounds

2a–2f were reacted with **4** in the presence of a catalytic amount of CuI in THF.

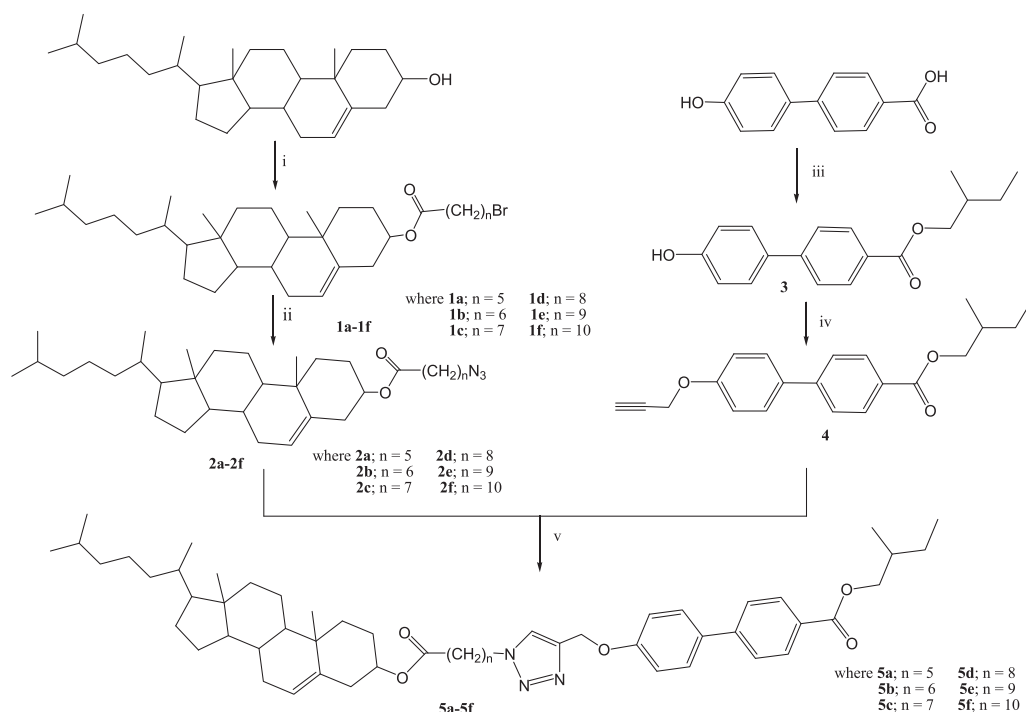
2.1. Thermal behavior study

Table 1 summarizes the data related to the thermal behavior and the textures for the title compounds along with the enthalpy values for the phase transitions. This table apparently shows that compounds with the shortest alkyl spacers (**5a** and **5b**) exhibit enantiotropic SmA* and monotropic SmC*, while the members with longer spacers **5c**, **5d** and **5e** show monotropic SmA* and SmC*. However, the homologue with the longest spacer **5f** consisting of decyloxy exhibits enantiotropic N* and SmA phases instead of SmC* and SmA*.

The DSC thermogram for compound **5b** shows two endothermic peaks representing Cr-SmA* and SmA*-I transitions at temperatures of 126.4 °C and 149.8 °C, respectively during the heating cycle. While on cooling cycle, there are three exothermic peaks, which can be assigned to I-SmA*, SmA*-SmC* and SmC*-Cr transitions at 149.8 °C, 121.6 °C and 101.2 °C, respectively (Fig. 1a). The associated enthalpy values for these transitions can be quantified as 9.3 kJ mol⁻¹ (I-SmA*), 0.5 kJ mol⁻¹ (SmA*-SmC*) and 21.1 kJ mol⁻¹ (SmC*-Cr). However, on heating compound **5f** shows three endothermic peaks representing Cr-SmA, SmA-N* and N*-I transitions at 108.3 °C, 114.6 °C and 116.3 °C, respectively (Fig. 1b). The enthalpies associated with these transitions are 52.3 kJ mol⁻¹ (Cr-SmA), 3.5 kJ mol⁻¹ (SmA-N*) and 6.5 kJ mol⁻¹ (N*-I).

The texture observation on compound **5a** shows that on cooling from the isotropic phase, the SmA* phase emerged as bâtonnet (Fig. 2a), which coalesced to afford a fan-shaped texture (Fig. 2b). On further cooling, the SmA* transformed to SmC* with a typical broken fan-shaped texture (Fig. 2c).

Cooling compound **5b** by 2 °C min⁻¹ from an isotropic liquid resulted in the formation of focal conic fans, which co-exist with the region of homeotropic alignment over a temperature range of 28 °C (Fig. 3a). This phenomenon supports the presence of SmA* phase as observed in cholesterol analogues (S)2MBbip-4-Chol.^{10a}



Scheme 1. Reagents for the synthesis of non-symmetric dimer (i) Br(CH₂)_nCOOH, DCC, DMAP, DCM; (ii) Na₃N, DMF; (iii) \pm 2-methylbutanol, HCl; (iv) propargyl bromide, K₂CO₃, acetone; and (v) CuI, THF.

Download English Version:

<https://daneshyari.com/en/article/5215106>

Download Persian Version:

<https://daneshyari.com/article/5215106>

[Daneshyari.com](https://daneshyari.com)