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Preliminary communication

Unsymmetrical trimesogens exhibiting the undulated twist grain boundary (UTGBC*) mesophase

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A new set of trimesogens consisting of a cholesteryl ester, a biphenyl and an azobenzene mesogenic segment joined together through either odd–even, even–even or odd–odd central alkylene spacers has been synthesized and the liquid crystalline properties investigated. The trimesogens having even–even and odd–odd central alkylene spacers exhibit the undulated twist grain boundary phase (UTGBC*) mesophase over a temperature range of ~40–50°C.

Twist grain boundary (TGB) phases are known to occur at the transition from smectic A (SmA) or chiral smectic C* (SmC*) to chiral nematic (N*) or isotropic (I) phases. The TGB phase consists of blocks of smectic layers, the successive blocks being rotated by a constant angle to give a helical structure. The blocks are separated from one another by screw dislocations to form grain boundaries which themselves are periodic [1, 2]. Renn and Lubensky [2 (*a*, *b*)] proposed three different types of TGB phase, viz. TGBA, TGBC and TGBC* depending on whether the blocks are of smectic A (SmA), smectic C (SmC) or smectic C* (SmC*) type. So far only the TGBA and TGBC phases have been experimentally characterized [2 (*a*, *d*)].

More recently another interesting form of the TGB phase has been discovered, although there have been no theoretical predictions for the existence of such a phase. According to the proposed model [3], this new phase has a highly frustrated structure, being characterized by modulations in all three dimensions, with the two-dimensional undulation of the SmC*-like blocks lying orthogonal to the helix of the TGB structure; this phase has been named the undulated TGBC* (UTGBC*) phase. It must be remarked here that one of the characteristic optical features, namely the square grid pattern, observed for the UTGBC* phase has also been reported for another TGB phase termed the S-TGBC phase [4 *a*] or TGBC* phase [4 (*b*–*e*)]. As the structural characteristics of neither of these phases have been clearly identified, we cannot presently assign a unique label to the type of phase observed in the materials reported in this paper. However our materials show, as we shall see later, optical textures with undulatory patterns. Hence we shall refer to the phase with such a character as a UTGBC* phase.

The UTGBC* phase was initially stabilized in a binary mixture of chiral and achiral molecules which have similar molecular structures [3 (*a*)]. This was followed by the observation of such a mesophase in a cholesterol-based single component system [5]. We have recently reported the synthesis and thermal behaviour of the first unsymmetrical trimesogen (which we refer to as CII-105), that comprises a cholesteryl ester, a tolan and an azobenzene mesogenic segment connected by central even–odd (C_4-C_5) parity alkylene spacers [6]. Surprisingly, this oligomer stabilizes the UTGBC* phase over a wide temperature range of ~90°C. Such an observation invites systematic investigations in order to understand the underlying structure–property relationship. To begin with we intended to replace the tolan (diphenylacetylene) segment in CII-105 with a biphenyl unit and also to vary the length of the two central alkylene spacers to realize new unsymmetrical trimesogens.

Here we report the synthesis and characterization of novel unsymmetrical trimesogens **1**, **2** and **3** consisting of a cholesteryl ester, a biphenyl and an azobenzene mesogenic moiety separated by either even–odd (C_4-C_5), even–even (C_4-C_4), or odd–odd (C_3-C_5) parity alkylene central spacers, respectively. The unsymmetrical trimesogens **1**, **2** and **3** were obtained by condensing unsymmetrical dimesogens **4a–c** with 4-*n*-butyl-4′-hydroxyazobenzene (**5**). The dimesogens **4a–c** were obained from

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cholesterly ω-bromoalkanoates (**6a–b**). The synthetic and other characterization-related studies will be published in detail elsewhere. The molecular structures of the target compounds and their intermediates (figure 1) were authenticated by spectroscopic (FTIR, ^{1}H and ^{13}C NMR, and FAB MS) analyses.

The mesomorphic properties of the trimesogens **1**, **2** and **3** were examined by polarizing optical microscopy and differential scanning calorimetry. We employed a Leitz DMRXP microscope equipped with a Mettler FP90 hot stage for optical textural observations and a Perkin-Elmer DSC-7 for calorimetric studies. Optical observations were made with glass slides, treated either for homogeneous alignment or for homeotropic alignment of the molecules. The results are summarized in the table. While cooling from the isotropic phase the unsymmetrical trimesogen **1** shows chiral nematic (N*), TGB, SmA, and SmC* phases, in addition to an as yet to be characterized liquid crystalline phase which we refer to as X, just below the SmC* phase. An important feature to be noticed is the absence of the UTGBC* phase. Thus the replacement of the tolan unit in CII-105 with the biphenyl core destabilizes the UTGBC* phase, indicating the sensitivity to molecular structure for such systems.

In order to determine whether the spacer parity influences the stability of the UTGBC* phase, we synthesized trimesogens **2** and **3** in which the three mesogenic segments are joined by either even–even (C_4-C_4), or odd–odd (C_3-C_5) parity alkylene spacers, respectively. The trimesogen **2** placed in a cell treated for planar orientation, shows on cooling from the isotropic phase the chiral nematic (N*) mesophase at ~220°C; this then changes to the TGB phase at ~213°C and this exists till ~202°C, before transforming to a third mesophase. On further cooling the sample crystallizes ~153°C. In a wedge-type cell with a similar surface treatment, Grandjean Cano dislocation lines are observed in the

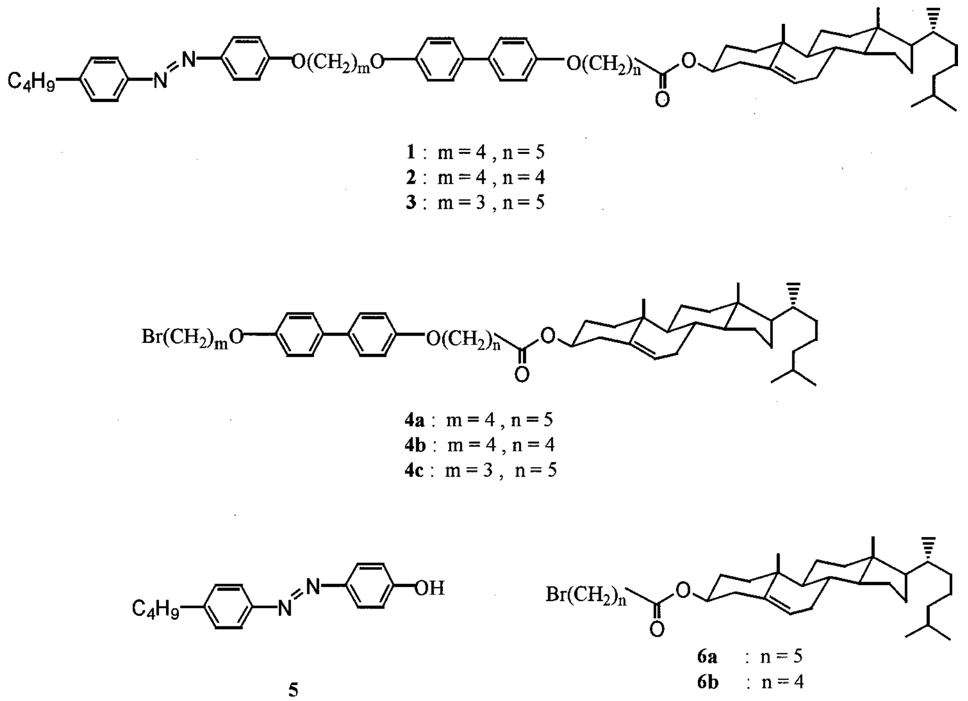
Table. Transition temperatures (°C) and enthalpies (J g^{-1}) of the unsymmetrical trimesogens. The enthalpy values are enclosed in brackets. I = isotropic liquid; N* = chiral nematic phase; TGB = twist grain boundary phase; UTGBC* = undulated twist grain boundary phase; SmA = smectic A phase; SmC* = chiral smectic C phase; X = unknown phase; Cr = Crystal.

Compound	Phase transition sequence[a]
1	I 239.3 (10) N* 229.6 (0.4) TGB[b]–SmA 211.4[c] SmC* 183.4[c] X 147.4 (28.8) Cr
2	I 220.4 (5.9) N* 213.7 (1.1) TGB 202.5[c] UTGBC* 153.8 (32.1) Cr
3	I 197.6 (4.6) N* 184.2 (2.6) TGB[b]–SmA 171.9[c] UTGBC* 128.4 (28) Cr

[a] Peak temperatures in the DSC thermograms obtained during heating cycles at 5°C min^{-1}.

[b] TGB is here a transient phase.

[c] Phase transition was observed by polarizing optical microscopy, but was too weak to be recognized by DSC.



1 : m = 4 , n = 5
2 : m = 4 , n = 4
3 : m = 3 , n = 5

4a : m = 4 , n = 5
4b : m = 4 , n = 4
4c : m = 3 , n = 5

5

6a : n = 5
6b : n = 4

Figure 1. Molecular structures of the unsymmetrical trimesogens **1–3** and their synthetic intermediates **4a–c**, **5**, **6a** and **6b**.

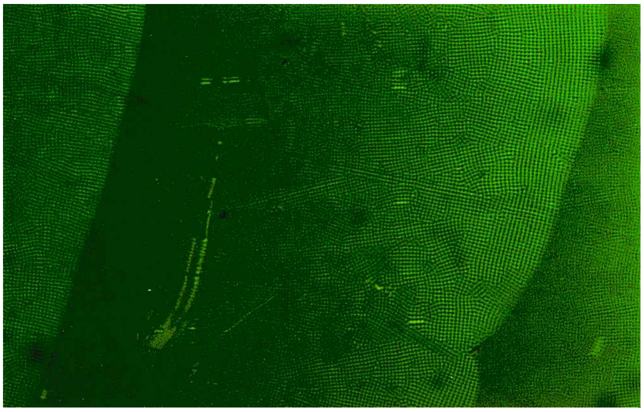


Figure 2. Photomicrograph (magnification ×320) obtained for the UTGBC* phase at 201.4°C while cooling from the TGB phase of trimesogen **2**. The sample was placed in a wedge-type cell with the glass plates treated for planar orientation. Notice the Grandjean Cano dislocation lines superposed on the square grid pattern.

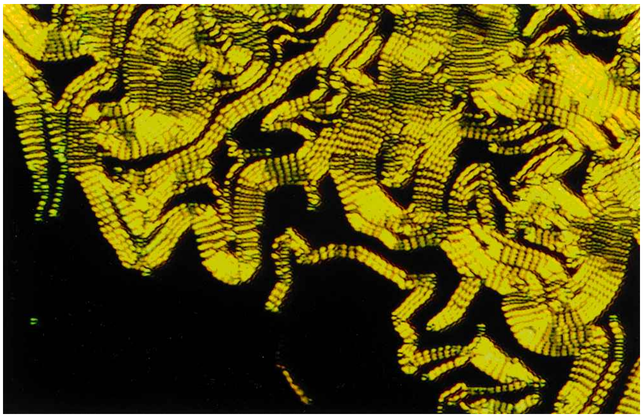


Figure 3. Photomicrograph (magnification ×320) of the undulated filament texture obtained in the UTGBC* phase at 200°C while cooling from the TGB phase of trimesogen **2** placed in a cell treated for homeotropic orientation.

N*, in the TGB phase and also in the third mesophase, demonstrating that there is a helical twist normal to the plates in these phases. The third mesophase shows, in addition, a square grid pattern superposed on the Grandjean Cano lines (figure 2). These textures are highly reproducible during any number of heating and cooling cycles. When the glass plates are treated to give homeotropic alignment, an undulated filament texture (figure 3) is observed whose periodicity is approximately the same as that of the spacing in the square grid pattern mentioned above. The features described here for the third mesophase are characteristic of the undulated twist grain boundary (UTGBC*) phase. Thus the trimesogenic compound **2** exhibits the UTGBC* phase over an approximately 48°C temperature range which, though wide, is less than that observed for CII-105. The trimesogen **3**, in which the three mesogenic segments are separated by odd–odd paraffinic spacers also gives a stable UTGBC* over a wide range of ~43°C, in addition to exhibiting SmA, TGB and N* mesophases. Note however that the temperature marking the upper range of stability of the UTGBC* phase is considerably lower for **3** (see table) than for compound **2**. The textures observed in the UTGBC* in this compound are identical to those seen for compound **2**.

In summary, we have synthesized new unsymmetrical trimesogens consisting of a cholesterly ester, a biphenyl and an azobenzene segment separated by either odd–even, even–even or odd–odd central alkylene spacers. Interestingly, trimesogens having even–even and odd–odd central spacers exhibit UTGBC* mesophase over temperature ranges of ~40–50°C. Our studies clearly indicate that, in such types of trimesogen the molecular structure of the three mesogenic segments and the length of the two central paraffinic spacers are critical for stabilizing the UTGBC* phase.

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