Liquid Crystal Abrikosov Flux Phase: The Exclusive Wide Thermal Range Enantiotropic Occurrence

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Liquid crystals (LCs) are orientationally ordered fluids formed by shape-anisotropic organic molecules.[1a,b] Since their discovery, molecular chirality and optical activity have become increasingly important aspects of research work in these ordered fluid systems.[1c] This is because the introduction of chirality to LC systems changes their structures by breaking mirror symmetry that has led to the discovery of a variety of frustrated fluid superstructures in addition to the technologically promising phenomena such as thermochromism and ferroelctricity. Twist grain boundary (TGB) phases,[2−5] theoretically considered as a LC analog[2a] of the type-II Abrikosov flux lattice,[2b] are frustrated phases usually stabilized by the molecules with high optical purity coupled with strong molecular chirality. In TGB phases, namely, TGBA, TGBC, and TGBC*, slabs of molecules which have local smectic A (SmA), smectic C (SmC), and chiral smectic C* (SmC*) structures, respectively, are rotated with respect to each other by screw dislocations resulting in the formation of a helical structure.[2−5] In general, TGB phases are known to exist at the phase transition from the isotropic liquid (I) or chiral nematic (N*) to smectic A or smectic C phases over a narrow temperature interval of a few degrees Celsius. Goodby and co-workers were the first to demonstrate the existence of the TGBA phase in a phase sequence I−TGBA−SmC* formed by a series of biphenyl esters.[3] Since then many new molecular systems showing the TGBA phase in different but interesting sequences such as I−BP−TGBA, I−TGBA−SmA−SmC*, I−BP−N*−TGBA, I−N*−TGBA−SmC*, I−BP−N*−TGBC−SmC*, I−BP−N*−TGBA−SmA−SmC*−SmX, I−BPIII−BPII−BPI−TGBA−TGBC−SmC*, and so forth have been reported.[4] Thus, the TGB phases have been observed hitherto to exist along with other types of mesophase.

Herein we report the first exclusive and independent occurrence of TGB phases over a remarkably wide thermal range discovered in several unsymmetrical LC dimers derived from cholesterol. The molecular structures of the three nonsymmetrical dimers **1a**, **1b**, and **1c** (see Supporting Information for details) investigated in this study have been shown in Chart 1 along with a space filling model of dimer **1a** in its all-trans (energy minimized) conformation. LC property of these compounds studied with the aid of optical polarizing microscope and differential scanning calorimeter (DSC; see Supporting Information for thermograms) are summarized in the Table 1.

The crystalline compounds **1a**, **1b**, and **1c** placed on clean glass slides were heated to the isotropic state and when cooled slowly (at a rate of 2 °C/min), and the transitions to the TGB mesophase occur at 123.2, 124.2, and 124.1 °C respectively, with a textural pattern identical to the one observed by Goodby and co-workers.[3] The usage of ordinary slides made it possible to visualize the textural patterns arising due to both homogeneous (planar) and homeotropic alignment of the molecules. Initially, the mesophase grows as droplets that on slight cooling further begin to coalesce to a pattern as shown in Figure 1a for the dimer **1b** as a representative case. On further cooling, the Grandjean planar (with a dull gray background) as well as a blurred pseudo-focal conic fan textures were observed in different regions of the slide. More importantly, at the edges of slide and also around the air packets, filaments were found to occur predominantly (see Figure 1b) which is the conclusive evidence for the presence of the TGB phase.[2c,3] When thin samples were examined in slides treated for planar condition, which orients the molecular long axis parallel to the substrate and thus the smectic layer planes perpendicular to the glass plates, as expected, Grandjean planar texture with a dull gray colored background was observed. Whereas when these compounds were confined to a thin cell with homeotropic anchoring conditions in which the molecules orient with their long molecular axis perpendicular to the substrates and, hence, the helix axis lying in the plane of the bounding glass plates, a beautiful filament texture is seen which in the majority of the area coalesces to a sort of fanlike texture as temperature is lowered in the TGB phase.

Preparation of a sample occured in a wedge cell treated for planar geometry, in which, due to continuous variation (increase) in the thickness of the cell from one end to other,

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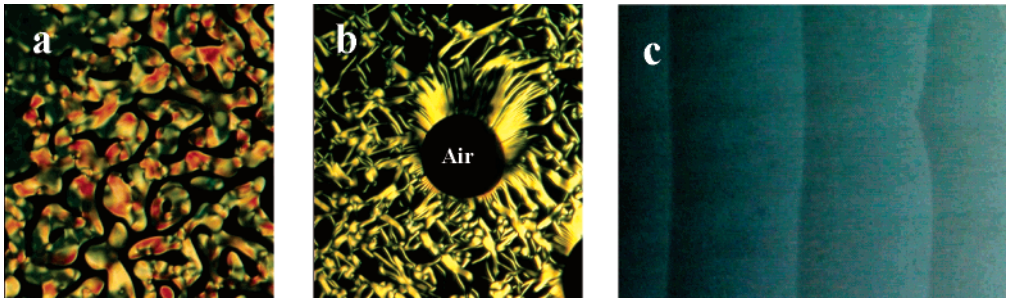
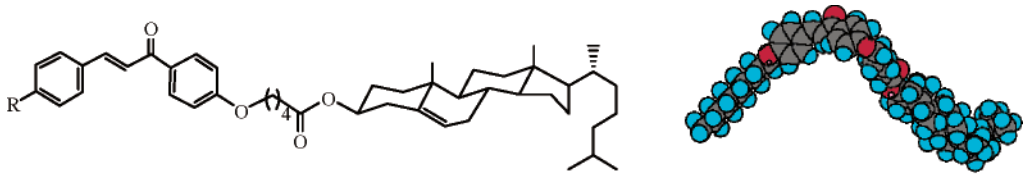


Figure 1. Photomicrographs of the TGB phase observed at different regions and substrate conditions for the dimer **1b**: (a) coalescence of the droplets separated from the isotropic phase (at 124 °C, ordinary slide); (b) filament textural pattern formed around the air packet (124 °C, ordinary slide); and (c) GC lines (at 120 °C, under planar anchoring conditions in a wedge cell preparation)

Chart 1



1a : R = $OC_{10}H_{21}$; **1b** : R = $OC_{11}H_{23}$; **1c** : R = $OC_{12}H_{25}$

Table 1. Transition Temperatures (°C)[a] and Enthalpies (J/g) of Unsymmetrical LC Dimers

dimer	heating	cooling
1a	Cr 118.9 (46)	I 123.2 (6.2)
	TGB 124.4 (6.2) I	TGB 104.4[b]
		TGBC* 81.6 (20.2) Cr
1b	Cr 114.2 (41.1)	I 124.2 (7.7)
	TGB 125.4 (7.8) I	TGB 110.2[b]
		TGBC* 83.6 (23.9) Cr
1c	Cr_1 114.2 (29)	I 124.1 (7)
	Cr_2 116.3 (8.6)	TGB 113.6[b]
	TGB 125.9 (7) I	TGBC* 82.5 (16.3) Cr

[a] Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at 5 °C/min. [b] The phase transition was observed under the polarizing microscope but was too weak to be recognized in DSC. I = isotropic liquid state; TGB = twist grain boundary phase that can have either SmA or SmC slabs; TGBC* = twist grain boundary phase having SmC* slabs; Cr_1 and Cr_2 = crystal.

an array of equidistant Grandjean−Cano (GC) dislocation lines (striations running from the top to bottom of the pattern) were formed in the TGB phase (Figure 1c). All these optical observations unambiguously ascertain the exclusive occurrence of the TGB phase[3,4a,6] in these materials, making them the first examples of TGB LCs (just as the nematic or chiral nematic N* or smectic LCs).[3,7,8] On cooling further, the TGB phase transforms into a more recently discovered TGB (with smectic C* blocks; TGBC*) mesophase[4a,9−11] at about 104, 110, and 113 °C respectively for the dimers **1a**, **1b**, and **1c** (see discussion to follow for details). Thus, these dimers stabilize the TGB phase over a wide temperature range, namely, 5−11 °C and 10−18 °C during the heating and cooling cycles, respectively, which is remarkable in view of the fact that in all known single component systems the thermal range of TGB phase rarely exceeds a few degrees Celsius.[4a,8]

For the TGBC* phase several different structures are possible due to the local SmC* tilt of the molecules.[4a,9−11] However, the occurrence of the square grid pattern for the planar anchoring condition seems to be a good evidence for the TGBC* structure proposed by Renn,[9] in which, in addition to the occurrence of a helical superstructure due to the TGB helix, the SmC* blocks exhibit the director helix of the bulk SmC* phase, with the helix axis perpendicular to that of the TGB helix. Another structure has been proposed for this phase to which authors refer to as the undulated TGBC* (UTGBC*) phase owing to the undulated nature of the smectic layers.[11] As the structure has not been clearly identified, the label TGBC* has been followed in this presentation. Experimentally it has been found that the TGBC* or UTGBC* phase exhibits a square grid pattern superimposed on the planar texture as expected. These dimers when investigated in slides treated for planar alignment and cooled from the planar texture of the TGB phase exhibit the TGBC* phase which showed a well-aligned square grid pattern as shown in Figure 2a. To ascertain that the square grid pattern observed is not due to some instabilities in the chiral smectic C* (SmC*) phase, these dimers were studied in wedge-shaped cells. During cooling from the TGB phase with GC lines, at the transition to TGBC* phase, a square grid pattern appears over these dislocation lines and fills the entire field of view as shown in Figure 2b. The GC lines indicate the presence of the TGB helical superstructure (twist axis perpendicular to the substrate) whereas the square grid patterns originate from the two-dimensional director modulation in the plane of the substrate, presumably due to the SmC* pitch. The simultaneous existence of both features is

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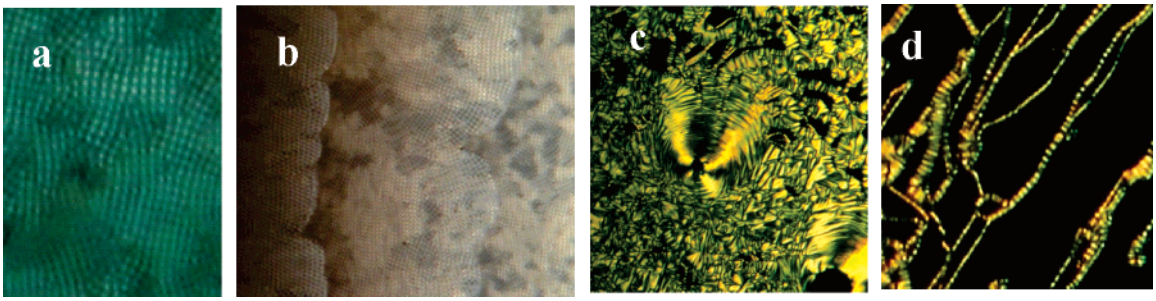

Figure 2. Microphotograph of the textural patterns observed for the TGBC* phase of the dimer **1b**: (a) square grid pattern seen in slides treated for the planar anchoring condition at 110 °C and (b) GC lines superposed on the square grid pattern observed at 107 °C in a wedge-type cell with the glass plates treated for planar orientation. (c and d) Undulated filament texture obtained in a cell treated for homeotropic orientation at 100 °C.

supposed to be the proof of the existence of the TGBC* phase. On the other hand, when examined on slides treated for homeotropic anchoring conditions and cooled from the filament texture of the TGB phase, transition to the TGBC* phase in which the filaments get undulated occurs. As a representative case, Figure 2c shows the undulated filament textural pattern of the TGBC* phase observed for the dimer **1b** in the same sample region as in Figure 1b. A similar pattern seen in another region of the slide is also shown in Figure 2d. In view of the fact that the TGBC* phase is a highly frustrated phase, its monotropic occurrence in the thermal range of 22−30 °C in these dimers is noteworthy. It is apparent that the thermal range of the TGB phase gets reduced with the enhancement in the temperature range of the TGBC* phase as the length of the terminal tail is increased.

Thus, dimers **1a**, **1b**, and **1c** exhibit a new LC phase sequence, namely, I−TGB−TGBC*, in which both the phases occur over wide temperature ranges. It is worth mentioning here that the phase sequence as well as transition temperatures are highly reproducible for any number of heating and cooling cycles. The unusual and remarkable thermal behavior of these dimers can be attributed to the dependence of the molecular shape on the parity of the spacer considered in the all-*trans* conformation. It is well-known that dimers with the odd central spacer adopt a bent conformation whereas those with an even spacer adopt a linear conformation.[12] Thus, the molecular shape of dimers **1a**−**c** possessing a C_5 spacer (the sum of four methylene units and one carbonyl carbon atom) is bent. Additionally, the chalcone mesogenic segment is a nonlinear core, which augments the twist in the overall shape of the molecule (Chart 1). This unusual and pronounced bent conformation of the molecules may be speculated to cause frustration of layer ordering. The formation of helical arrangement of the smectic domains to form the TGB phase (with the axis of the helix perpendicular to the long axes of the constituent molecules) could relieve this frustration.[13] Further, the decrease in the temperature of this structure possibly enhances the frustration in the smectic layers to give the TGBC* phase. Significantly, this finding is not a trivial one, thus necessitating a rational approach from both theoretical and experimental viewpoints.

In conclusion, we have discovered the first examples of LCs exhibiting the TGB phases exclusively. The stabilization of frustrated fluid phases by chiral dimers with high enantiomeric excess and strong molecular chirality synthesized in the present investigation is a consequence of the frustration of layer structure due to the pronounced bent molecular conformation of the constituent dimers that is relived by the formation of helical structure. This remarkable finding opens a lot of new prospects of the TGB materials and invites systematic investigations in the area of chiral LCs.

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Supporting Information Available: General experimental details, scheme depicting the synthetic steps employed to obtain the unsymmetrical dimers and their precursors, characterization data, and DSC thermograms (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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