Twist-grain-boundary transitions in a chiral tolane compound

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High resolution calorimetric studies have been carried out on the chiral compound methylheptyloxydifluorooctyloxybenzoyloxytolane ($8\text{FBTFO}_7$). The tilt tendency is greater in this compound than in several other similarly structured fluorinated tolane liquid crystals, and it exhibits tilted chiral smectic C (SmC*) and tilted twist-grain-boundary (TGBc) phases but not the untitled SmA or TGBa phases. The data confirm the presence of two tilted TGBc phases denoted TGBb and TGBa. The TGBb and TGBa first-order transition exhibits considerable hysteresis and a very small latent heat. There is no rounded excess heat capacity peak in the cholesteric N* phase associated with the non-transitional evolution of a chiral line liquid NL, although such a feature has been observed in other fluorinated tolanes with a smaller tilt tendency.

1. Introduction

During the past ten years, there have been numerous studies of chiral liquid crystals that exhibit twist-grain-boundary phases with a regular stack of periodic grain boundaries separating regions of smectic A order (TGBa) or tilted smectic C order (TGBc). These phases were predicted theoretically by Renn and Lubensky [1, 2], and the TGBa phase was first observed experimentally by Goodby and coworkers [3–5]. Of special interest are investigations of several homologous series of fluorinated compounds with a tolane core and having the general formula

$$C_n\text{H}_{2n+1}O\text{-}COO\text{-}\text{C}==\text{C}\text{-}O\text{-}\text{C}\text{H}_3$$

The series denoted as $n\text{FBTFO}_7$, where $X = F$ and $Y = Z = H$, is 3-fluoro-4[(R) or (S)-1-methylheptyloxy]-4’-(4-alkoxy-3-fluorobenzoyloxy)tolane. These compounds display primarily a TGBa phase [6] with a very narrow TGBc range for $n \geq 12$ [7]. This TGBa phase and associated transitions have been well characterized structurally [6] and calorimetrically [8]. The homologous series $n\text{F}_2\text{BTFO}_7$, where $X = Y = F$ and $Z = H$, is the 2,3-difluorobenzoyloxy analogue of $n\text{FBTFO}_7$. These compounds exhibit both the TGBa phase ($n < 11$) and the TGBc phase ($n > 10.5$); the TGB structures and transitions have been extensively studied [9–12]. The series $n\text{BTFO}_7$, where $X = Y = H$ and $Z = F$, exhibits TGBc and SmC* phases but no TGBa or SmA phases and monotropic ferro- as well as antiferro-electric smectic C* phases have also been observed just above room temperature [13, 14]. Thus the tilting tendency for a given alkoxy chain length increases as one goes from $n\text{FBTFO}_7$ to $n\text{F}_2\text{BTFO}_7$ to $n\text{BTFO}_7$.

High-resolution calorimetric studies of $n\text{FBTFO}_7$, $n\text{F}_2\text{BTFO}_7$, and $n\text{BTFO}_7$ compounds [8, 12] have revealed two interesting features that are not yet fully understood. First, there is a large rounded excess heat capacity peak in the cholesteric region that has no associated transitions and associated transitions have been well characterized structurally [6] and calorimetrically [8]. The homologous series $n\text{F}_2\text{BTFO}_7$, where $X = Y = F$ and $Z = H$, is the 2,3-difluorobenzoyloxy analogue of $n\text{FBTFO}_7$. These compounds exhibit both the TGBa phase ($n < 11$) and the TGBc phase ($n > 10.5$); the TGB structures and transitions have been extensively studied [9–12]. The series $n\text{BTFO}_7$, where $X = Y = H$ and $Z = F$, exhibits TGBc and SmC* phases but no TGBa or SmA phases and monotropic ferro- as well as antiferro-electric smectic C* phases have also been observed just above room temperature [13, 14]. Thus the tilting tendency for a given alkoxy chain length increases as one goes from $n\text{FBTFO}_7$ to $n\text{F}_2\text{BTFO}_7$ to $n\text{BTFO}_7$.

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was reported. The present investigation involves a high-resolution calorimetric study of $8\text{BTFO}_2\text{O}_4\text{M}_4$. This system is of interest since the tilting tendency is significantly larger than in the related compounds $n\text{FBTFO}_2\text{M}_5$ and $n\text{F}_2\text{BTFO}_3\text{M}_5$, i.e., there are no TGB$_4$ or SmA phases. Furthermore, both the N* range and the TGB$_c$ range (especially that of TGB$_2$) are much wider than those of analogous phases in 11F$_2$ BTFO, M$_5$ and 12F$_2$ BTFO, M$_5$. Our calorimetric data show no indications of a rounded N*-N$_t$ excess heat capacity feature, which agrees well with the previously reported trend of decreasing N*-N$_t$ enthalpy as the tilt tendency increases [12]. The presence of a first-order TGB$_2$-TGB$_1$ transition has been confirmed on both heating and cooling scans.

2. Experimental results

The compound 2BTFO$_2$O$_4$M$_4$ ($\delta$-1-methylheptyloxy]-2,3-difluoro-4'-(4-octyloxybenzoyloxy)tolane, with a molecular weight of 590.7 g mol$^{-1}$, was synthesized at the Centre de Recherche Paul Pascal following the procedure described in [14]. The S enantiomer investigated here is the same enantiomer that was studied in [14]. The reported phase sequence [13, 14] on the basis of DSC scans is

$$K \rightarrow \text{SmC}^* \rightarrow \text{TGB} \rightarrow \text{TGB} \rightarrow \text{N}^* \rightarrow \text{BP} \rightarrow \text{I}$$

where the transition temperatures in Kelvin are values obtained on heating (except for the monotropic transitions which were obtained on cooling scans). Preliminary DSC heating scans at $+0.5$ K and $+1$ K min$^{-1}$ were carried out on the 8BTFO, O$_4$M$_4$ sample used in the present study, the transition temperatures agreeing well (within $\pm 0.4$ K) with those cited above. On the basis of a comparison of DSC transition temperatures with those obtained with high-resolution ac calorimetry, it appears that there is a calibration error in the DSC thermometry. We estimate that the DSC temperatures are $\sim 0.75$ K lower than the true values. This systematic DSC calibration error is comparable to the value of $\sim 1$ K observed for $n\text{FBTFO}_2\text{O}_4\text{M}_5$ [16].

The present study covered the 330–400 K temperature range, but detailed measurements were focused on the SmC*-TGB$_2$-TGB$_2$-N* region. This notation used in [14] for the TGB$_c$ phases of 8BTFO$_2$O$_4$M$_4$ will be retained. Although it is quite possible that there is an isomorphism between these TGB$_2$/TGB$_4$ phases and the TGB$_c$/TGB$_4$ phases of $n\text{FBTFO}_2\text{O}_4\text{M}_5$ [12], it seems better to use different notations to allow for the possibility that different structures are involved.

A small mass (26 mg) of 8BTFO$_2$O$_4$M$_4$ was degassed under vacuum and then cold-weld sealed into a thin silver cell. Thermal measurements were carried out in a computerized calorimeter capable of automated operation in either an ac mode or a ramped relaxation mode called non-adiabatic scanning (nas). This calorimeter and the appropriate equations for analyzing the observed $T_n$ response to the $P_o \exp(i\omega t)$ ac heat input or the observed $dT/dt$ response to a linearly ramped dc heater power input are described elsewhere [17]. The essential difference between the two modes of operation is that the ac mode measures heat capacity $C_p$ directly and is capable of very slow scan rates. However, it can at best provide only qualitative information about the presence of a two-phase coexistence region at a first-order transition. The nas mode measures the enthalpy $H$ as a function of temperature and thus yields both $C_p$ values in one-phase regions and latent heats at first-order transitions. The procedure for a nas run was as follows. The bath temperature was stabilized $\sim 1.5$ h at an initial value and held constant at this value during a pair of scans; the dc heater power to the sample was first ramped down to zero over 500 s (resulting in a cooling of $\sim 0.96$ K); after a $\sim 500$ s waiting period for sample temperature equilibration, the heater power was ramped up over 500 s (resulting in a heating of $\sim 0.96$ K). Following this sequence, the bath temperature was set at a new lower value and stabilized there for $\sim 1.5$ h prior to carrying out another pair of scans.

On the initial ac heating scan, a sharp melting transition was observed at 336.04 K, in good agreement with the value reported by Navailles et al. [13, 14]. An overview of $C_p(ac)$ data obtained on a later scan for the range 350–400 K is shown in figure 1. These data were obtained at an a.c. frequency $\omega = 2 \omega_0$, where $\omega_0 = 2\pi f_0 = 0.196$ s$^{-1}$ (or $f_0 = 31.25$ mHz) is the standard operating frequency previously used with this calorimeter. The data in figure 1 were obtained on heating at a scan rate of $+0.2$ K h$^{-1} = +3.3$ mK min$^{-1}$. The transitions that are obvious from figure 1 are TGB$_2$-N* at 360.45 K and BP–I at 396.0 K. Both these transitions undergo a downward drift in the transition temperature dependent on the length of time that the sample is held at high temperatures. The drift rate is quite rapid (about $-0.2$ K day$^{-1}$) during the first few days and then becomes much slower ($-3$ mK day$^{-1}$) for longer periods. Analogous drifts in transition temperatures were also observed for $n\text{F}_2\text{BTFO}_2\text{O}_4\text{M}_5$ compounds [12]. Since the data in figure 1 were obtained on run 5 after 30 days at temperatures above 350 K, we estimate the transition temperatures extrapolated back to $t = 0$ are 361.85 K for TGB$_2$-N* and 399.3 K for BP–I. These ‘zero-time’ transition temperatures agree well with the corrected DSC values from [14] and those obtained at MIT. A confirmation of these zero-time extrapolated values is the fact that the TGB$_2$-N* transition was observed at...
361.85 K on the first heating run, where any drift is negligible due to the short time the sample had been at high temperatures.

Anomalies in the phase shift between \( T_{ac}(\omega) \) and \( P_{ac}(\omega) \) indicate two-phase coexistence at a first-order transition and interphase conversion during the \( T_{ac} \) oscillation \([17]\). Such anomalies were observed at both the TGB\(_2\)–N* and the BP–I transition. Heat capacity points in figure 1 that are frequency-dependent apparent values obtained in a two-phase coexistence region are denoted by the symbol \( \times \). All other \( C_p(\text{ac}) \) data points are frequency independent (as judged by comparing data obtained at 2\( \omega_0 \) and \( \omega_0/2 \)) and exhibit no phase shift anomalies.

The most important aspect of the data in figure 1 is the absence of any broad rounded excess \( C_p \) peak in the middle of the N* phase. This disappearance of a N*-N\(_f\) feature will be discussed in §3.1. A more detailed study of the N*-BP–I region reveals a small excess \( C_p(\text{N}^*-\text{BP}) \) peak \( \sim 0.35 \) K below the large BP–I peak, but the behaviour in this region will not be discussed further.

Figure 2 provides a more detailed view of calorimetric data in the SmC*-TGB–N* region. Shown in figure 2(a) are \( C_p(\text{ac}) \) data obtained on a cooling run at frequency \( \omega_0/2 \) and a scan rate of \( -0.135 \) K h\(^{-1}\). Figure 2(b) shows non-adiabatic scan (nas) data obtained from cooling ramps with \( dT/dt \approx -6.9 \) K h\(^{-1}\) = \( -0.115 \) K min\(^{-1}\). Note that these ramp rates are much slower than DSC scan rates \( (0.5\text{--}1.0 \) K min\(^{-1}\) \) but much faster than ac scan rates. Comparison of figures 2(a) and 2(b) shows that both ac and nas data clearly show the prominent TGB\(_2\)–N* first-order transition with \( C_p(\text{nas}) \geq C_p(\text{ac}) \) in the two-phase coexistence region. Also there is a small excess \( C_p(\text{nas}) \) peak at the TGB\(_2\)–TGB\(_1\) transition which is not observed in the \( C_p(\text{ac}) \) data. Both these features are analogous to those observed in a high-resolution study of N*-BP–BP\(_{\text{III}}\)–I transitions in a highly chiral liquid crystal without TGB phases \([18]\). \( C_p(\text{ac}) \) data as a function of \( \Delta T = T - T(\text{TGB} - \text{N*}) \) was the same on heating and cooling runs, but the \( C_p(\text{nas}) \) data differed on heating and cooling in the TGB\(_2\)–TGB\(_1\) region.

Figure 3 shows the hysteresis in the TGB\(_1\)–TGB\(_2\) transition observed in the nonadiabatic scanning data. On cooling, the width of the TGB\(_1\) phase, \( T(\text{TGB} - \text{N*}) - T(\text{TGB} - \text{TGB} - \text{TGB} - \text{TGB}) \), is 0.74 K and on heating it is 0.33 K (which is in good agreement with the value 0.4 K from DSC heating scans \([14]\)). Taking the midpoint of these heating and cooling transition temperatures, we estimate the ‘zero-time’ equilibrium transition temperature to be 361.32 K. Also shown in figure 3 is a solid line representing the \( C_p(\text{ac}) \) variation given in figure 2 and an arrow indicating the expected position.
of the SmC*-TGB$_1$ transition based on DSC heating scans carried out at MIT. Discussion of the thermal behaviour in the TGB$_1$–TGB$_2$ transition region and the absence of an excess heat capacity peak at the SmC*-TGB$_1$ transition will be given in §3.

Integration of the non-adiabatic scanning data as described in [8, 12, 18] yields a TGB$_2$–N* latent heat $L$ of 0.53 J g$^{-1}$ and one might also include the pretransitional enthalpy $\delta H = \int (C_p(ac) - C_p(background)) \, dT = 1.16$ J g$^{-1}$ associated with the $C_p(ac)$ ‘wing’ over a 25 K range above and below the TGB$_2$–N* transition. This total transitional enthalpy of $\sim 1.7$ J g$^{-1}$ can be compared with less accurate DSC values of 1.2 J g$^{-1}$ (MIT, +1 K min$^{-1}$ scan) or 0.485 J g$^{-1}$ ([14], +0.5 K min$^{-1}$ scan).

3. Discussion

3.1. Absence of N*-N$_l$ heat capacity peak

In contrast to the behaviour of $n$FBTFO, $M_7$ and $n$F$_2$BTFO, $M_7$ compounds, there is no indication of a broad and rounded N*-N$_l$ $C_p$ peak in 8BTFO, $O$, $M_7$. In the former compounds, the integrated enthalpy $\delta H$ of this feature is substantial, ranging from 1.8 J g$^{-1}$ in 9FBTFO, $M_7$ to 0.8 J g$^{-1}$ in 11FBTFO, $M_7$ and 1.4 J g$^{-1}$ in 10F$_2$BTFO, $M_7$ to 0.28 J g$^{-1}$ in 12F$_2$BTFO, $M_7$ [8, 12]. This marked decrease in $\delta H$ as the tilting tendency increases, and the complete absence of any analogous feature in 8BTFO, $O$, $M_7$, strongly suggests that any twist-grain-boundary ordering in the ‘N$_l$ phase’ of $n$FBTFO, $M_7$ and $-F_2$BTFO, $M_7$ is due to TGB$_A$-like structures.

The nature of the ‘N$_l$ phase’ is not yet resolved. In [8] and [12], it was proposed that there is a non-transitional evolution of short-range TGB order on cooling as N* converts into a chiral line liquid denoted as N$_l$. This N*-N$_l$ assignment is consistent with the thermal evidence for $n$FBTFO, $M_7$ and $n$F$_2$BTFO, $M_7$; no latent heat, and very broad (5–10 K) and very rounded excess heat capacity peaks that are nonsingular [8, 12]. However, a recent X-ray study of 10F$_2$BTFO, $M_7$ [11] indicates that this purported N$_l$ region may possibly be an incommensurate TGB$_A$ phase, followed at lower temperatures in that compound by a commensurate TGB$_A$ phase. Thus the sequence TGB$_A$(com)–TGB$_A$(inc)–N* with two thermodynamic transitions may occur in 10F$_2$BTFO, $M_7$ instead of TGB$_A$–N$_l$–N*.

The critical issue is whether or not the TGB$_A$ order is long range or short range in such a ‘N$_l$’ region. If a chiral line liquid N$_l$ does exist in 10F$_2$BTFO, $M_7$, the short-range TGB$_A$ order must be well developed since the excess N*-N$_l$(inc) phase [\[10\]–\[12\]] yields a TGB$_A$ phase of finite smectic slab thicknesses. It is important to check the smectic order along the pitch direction as well as in the plane perpendicular to the helical axis studied in [11]. If 10F$_2$BTFO, $M_7$ does exhibit a true transition from N* to TGB$_A$(inc), why is the associated excess heat capacity non-singular? It should be noted that the observed broad $C_p(T)$ variation is unlike that characteristic of typical finite-size truncation effects.

The interesting issue for 8BTFO, $O$, $M_7$ is not only the absence of a N*-N$_l$ rounded $C_p$ feature like that discussed above but also the clear presence of a conventional pretransitional excess heat capacity in the N* phase at temperatures above the TGB$_2$–N* transition. As shown in figure 1, this excess $C_p$ extends over $\sim 20$ K and the integrated enthalpy $\delta H'$ associated with this high-temperature $C_p$ wing is $\sim 0.5$ J g$^{-1}$, which is comparable to $\delta H$(N*-N$_l$) for 11FBTFO, $M_7$ and 11F$_2$BTFO, $M_7$. X-ray data in a 3 K range above $T$(TGB$_2$–N*) reveal diffuse scattering that corresponds to truly short range TGB$_C$-like ordering in the N* phase of 8BTFO, $O$, $M_7$ [14].

3.2. Two TGB$_C$ phases

Figure 3 confirms the existence of a TGB$_1$–TGB$_2$ transition between two TGB$_C$ phases as suggested by earlier data [14]. The high temperature TGB$_2$ phase
in 8BTF$_2$O$_4$M$_1$ is \( \sim 0.5 \) K wide, but the first-order TGB$_1$–TGB$_2$ transition is kinetically sluggish and there is a large hysteresis. An analogous pair of TGB$_b$ phases, denoted TGB$_b^2$ and TGB$_b^3$, has been reported in 11F$_2$BTFO$_4$M$_1$ and 12F$_2$BTFO$_4$M$_1$, although these TGB$_b$ phases have only a narrow range of stability (\( \sim 0.73 \) K for TGB$_b^2$ and \( \sim 0.06 \) K for TGB$_b^3$) [12]. These TGB$_b^2$/TGB$_b^3$ and TGB$_b$/TGB$_2$ pairs may well be structurally related but there are several differences in the thermal behaviour of 8BTF$_2$O$_4$M$_1$ and nF$_2$BTFO$_4$M$_1$. In contrast to the behaviour of 8BTF$_2$O$_4$M$_1$, TGB$_b$–TGB$_b^3$ transitions were clearly observed in ac calorimetry as low temperature shoulders on the TGB$_b$–N$_b$ heat capacity peak and as distinct ac phase shift anomalies, and, furthermore, no hysteresis was observed. Both these differences may be due to substantial differences in the rates of TGB$_b^2$–TGB$_b^3$ and TGB$_b$–TGB$_2$ phase conversion. However, there are also considerable differences in the transition enthalpies. For nF$_2$BTFO$_4$M$_1$, the latent heats for TGB$_1$–N$_1$, TGB$_1$–TGB$_2$, and TGB$_1$–TGB$_1$ transitions were \( 0.125 \pm 0.02 = 0.145 \) J g$^{-1}$ for \( n = 11 \) and \( 0.255 \pm 0.04 = 0.295 \) J g$^{-1}$ for \( n = 12 \) [12]. For 8BTF$_2$O$_4$M$_1$, \( L(TGB_1^b-N_1^b) = 0.53 \) J g$^{-1}$ and \( L(TGB_1^b-TGB_2^b) \) is estimated to be \( \sim 0.02 \) J g$^{-1}$. The latter value is very difficult to determine in view of the hysteresis and a sluggish conversion which suggests that some of the transition enthalpy is smeared out over almost \( 1 \) K.

A recent extension has been made of the mean field Chen–Lubensky theoretical approach used originally in [1, 2] to analyse the phase behaviour of chiral molecules. This new theoretical work of Luk’yanchuk [19] considers the stability of four structurally different TGB$_b$ phases. The TGB$_b^1$ and TGB$_b^2$ phases have SmC slabs (no director precession) where the tilted smectic layers of the analogous SmC*–TGB$_b^3$ phase have SmC slabs (no director precession) where the tilted smectic layers of the analogous SmC*–TGB$_b^2$ phase have SmC* slabs, and a evidence for this transition is from DSC heating scans. DSC scans yielded transition enthalpies of \( \sim 0.045 \) J g$^{-1}$ ([14], \( +0.5 \) K min$^{-1}$) to \( \sim 0.08 \) J g$^{-1}$ (MIT, \( +1 \) K min$^{-1}$).

A possible explanation of these observations is that the development of structural ordering in the TGB$_b$ phase is slow and, furthermore, the heat capacities of fully equilibrated SmC* and TGB$_b$ phases are essentially identical and the equilibrium latent heat is very small for this transition. If this were so, slow ac and nas scans would show no thermal evidence of this transition while rapid DSC heating scans would involve a transition from SmC* to a non-equilibrium TGB$_b$ state with higher disorder (and thus higher enthalpy) than the equilibrium TGB$_1$. In any event, optical pitch data and X-ray data both unambiguously indicate the presence of the SmC*–TGB$_b$ transition at \( \sim 360.5 \) K [14].

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8BTFO, M1 sample. This work was supported by the MRSEC program of the National Science Foundation under Grant No. DMR 94-00334.

References


[14] NAVAILLES, L., NGUYEN, H. T., BAROIS, P., ISAERT, N., and DE LORD, P., 1996, Liq. Cryst., 20, 653. It should be noted that there is a typographical error in the melting point reported here. It should be 62.4°C, not 52.4°C.


[20] DOZOV, I., 1995, Phys. Rev. Lett., 74, 4245. In this paper, the TGBa phase is called a twist-melted-grain-boundary (TMGB) phase, which emphasizes the fact that the smectic order parameter should vanish at the grain boundaries.