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HIGH PRESSURE STUDIES ON NEW CHIRAL COMPOUNDS EXHIBITING TGB$_A$ PHASE

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Abstract

Effects of high pressures on phase sequences of the two homologous $n=16$ and $n=18$ of the (3-fluoro-4 ((R) or (S)-methylheptyloxy) 4,(4''-fluoro benzoyloxy) tolans) series have been studied. Both compounds exhibit the new twisted Smectic A phase called Twist Grain Boundary TGB$_A$ phase. The high pressure experiments were performed by thermobarometric analysis. The order of the transitions (first or second) have been determined in respect to pressure and temperature. The pressure–temperature phase diagrams show that the TGB$_A$ phase is stabilized by increasing pressure; an induced N^* phase appears under high pressure for n=18 leading to the observation of TGB$_A$–N^*–I triple point.

Keywords: thermobarometric analysis, Twist Grain Boundary phase

Introduction

Great efforts that have been made by chemists during the last years, allowed to obtain new chiral mesogenic systems – which have led to the observation of a variety of phase sequences involving classical or/and new mesophases. For some of them, the molecular chirality induces an helicoidal structure. So, in Cholesteric (N^*) phase (Fig. 1b) – which is in fact twisted Nematic (N) phase (Fig. 1a) –, the long axis of the molecules (noted $\vec{n}$) rotates along an axis which is perpendicular to the molecules. Among layered structures – or Smectic (S) phases – for which common feature is the arrangement of the molecular centers in equidistant planes, are observed for chiral molecules, the S_A (Fig. 1c) and S_C^* (Fig. 1e) – which is in fact a twisted Smectic C phase (Fig. 1d) – where the molecular orientations are respectively perpendicular to the layers (S_A) and tilted with respect to the layer normal with the tilt direction rotating along a helical axis normal to the layers (S_C^*). Recently new types of twisted Smectic

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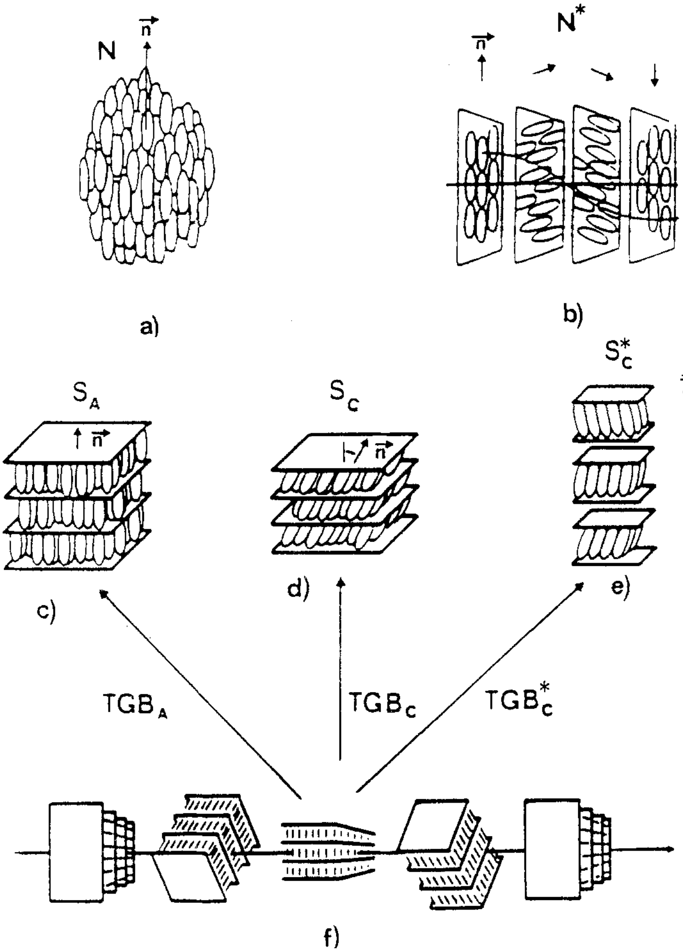


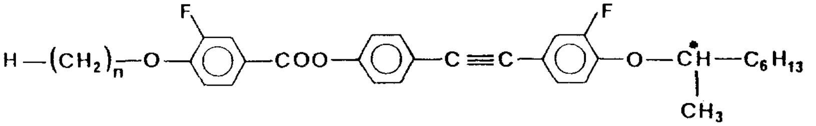
Fig. 1 Schematic representation of the structure of a) Nematic phase, b) Cholesteric phase, c) Smectic A phase, d) Smectic C phase, e) helical Smectic C * phase and f) Twist Grain Boundary phases

phases, called Twist Grain Boundary (TGB) phases have been predicted [1, 2]. In these phases the helical twist is obtained by rotations of Smectic blocs around an axis parallel to the layers (Fig. 1f). Between every pair of adjacent blocs, there exists a grain boundaries of screw dislocations which are regularly spaced along the TGB structure [1, 2]. According to the nature of molecular orientation within the Smectic blocs, distinctions can be made between three types of TGB phase: TGB$_A$, TGB$_C$ and TGB$_C^*$ corresponding respectively to S_A, S_C and S_C^* blocs. Experimentally, the TGB$_A$ and TGB$_C$ phases have been observed [3–5]. The known phase sequences with new TGB phases are K S_C^* TGB$_A$ I [6, 7], K S_C^* S_A TGB$_A$ N^* I [4, 8], K S_A TGB$_A$ N^* I [4, 9], K S_C^* TGB$_A$ N^* I [4] and K

S_C^* TGB$_A$ TGB$_C$ N^* I [5], where the symbols K and I denote Crystalline and Isotropic liquid phases. For chemical series, systematic variation of aliphatic chain lengths can considerably influence the stability and temperature ranges of TGB phases [3–5]. On the other hand, mixing experiments [2, 5, 8] carried out at atmospheric pressure on several binary systems of chiral mesogens, have shown the effect of the concentration on the appearance or disappearance of TGB phases on temperature–concentration (T–C) phase diagrams leading to singular points involving TGB phases such as triple points or multicritical points previously predicted by the Renn-Lubensky theory [2]. Changes in pressure can produce analogous effects of those observed by changes in the concentration for binary mixtures. Moreover, by studying the physical properties of liquid crystals under pressure one can obtain some insight into the intermolecular forces which give rise to the different mesophases. However, only few experimental studies have been carried out on the new TGB phases under high pressure. Thus, for example, we have reported in our earlier paper [10] the first pressure experiments on a new chiral mesogens which have led to the first observation of a S_C^*–S_A–TGB$_A$ multicritical point on pressure–temperature phase diagram. It is the purpose of this paper to present systematic high pressure studies up to about 160 MPa of two new chiral compounds exhibiting TGB$_A$ phase using thermobarometric analysis (T.B.A.). The principal goals of this work is to study the effect of pressure on the TGB$_A$ phase stability, on phase sequences involving this new type of mesophase and on the order of the transitions.

Compounds

We have chosen two chiral liquid-crystal compounds which both exhibit the TGB$_A$ phase. These compounds belong to the same chemical series of the two homologous recently studied under pressure by Anakkar and coll. [10]. This chemical series synthesized by H. T. Nguyen [4] is (3-fluoro-4 ((R) or (S)-methylheptyloxy) 4'-(4''-fluoro benzoyloxy) tolans) in short nFBTFO$_1$M$_7$. The general formula is:



This homologous series is very interesting for many reasons. It exhibits TGB$_A$ phases for all the synthesized homologous and TGB$_C$ ones for $n=12$, 13 and 14 homologous [11], and is then a suitable series for studying the evolution, versus pressure, of the phase sequences including TGB phases. Moreover, a rich mesomorphic polymorphism is observed which is sensitive to changes in alkoxy chain length leading to appearance or disappearance of mesophases from lower homologous to higher ones. Thus, high pressure studies of this series primarily revealed multicritical behaviours in P–T phase diagram involving the TGB phases and allowed to confirm the predictions of the Renn-Lubensky theory [2]. This paper concern high pressure measurements on $n=16$ and $n=18$ members of nFBTFO$_1$M$_7$. The phase sequences under atmospheric pressure are:

$n=16$ K 334 K S_C^* 371 K TGB$_A$ 372.3 K N^* 372.8 K I

$n=18$ K 339 K S_C^* 370.3 K TGB$_A$ 371 K I

The phase identifications and transition temperatures have been determined by A. Bouchta and coll. [4] by both thermal microscopy and differential scanning calorimetry. The cholesteric phase is not observed for $n=18$; so, it is very interesting to know, by analogy with reentrant phenomena (i.e. existence at lower temperature of a phase already stable at higher temperature) in polar homologous series [12, 13], whether the phase sequence under pressure for $n=18$ can become similar to the lower homologous; then, pressure would induce the cholesteric phase leading to a singular point in the P–T phase diagram. The $n=16$ member is also chosen for studying the behaviour of S_C^* TGB$_A$ N^* phase sequence under pressure.

Method

The phase transitions of both compounds were detected under pressure by thermobarometric analysis (T.B.A.) which consists in recording, versus temperature, the pressure (thermobarogram) of a small (about 10 mg) sample of mesogen enclosed in metallic cell [14]. The sample is introduced in the cell in crystalline powder, then melted in liquid phase and last recrystallized. All the phenomena that appears for liquid crystals are reversible and the thermal treatment has no influence in the following thermodynamic behaviour. Detailed descriptions of the method, the experimental set up (automated metabolemeter: SCERES, MAB 02A20), interpretation and exploitations of thermobarograms has been given elsewhere [15–17]. Measurements have been performed in the temperature range 323 to 433 K and for pressure up to about 160 MPa. All thermobarograms are obtained by heating, when varying the temperature at a rate of 0.5 K min^{-1}. Whatever the transformation, pressure of the equilibrium is given, for a given temperature and the scanning rates has not influence on the (P–T) values.

Results

Figures 2a–c and 3a–c give experimental thermobarograms obtained for $n=16$ and $n=18$. Several systems of thermobarograms have been recorded by changing the initial experimental conditions for pressure and temperature. For $n=16$, all the thermobarograms exhibit, at the S_C^*–TGB$_A$ transition, a weak

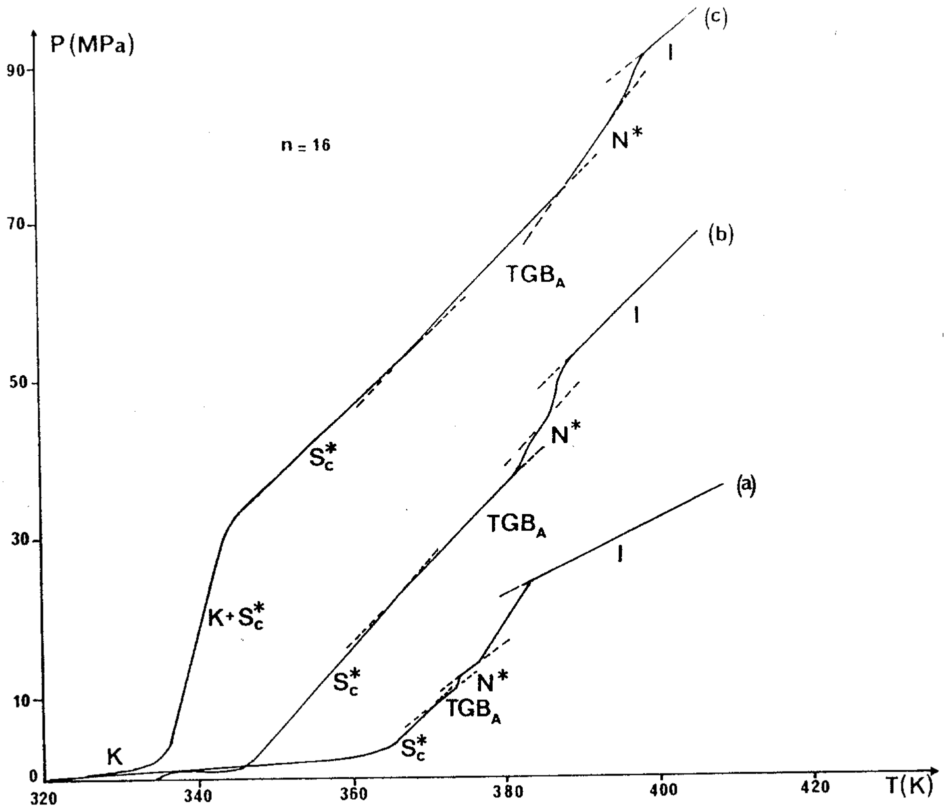


Fig. 2 Examples of thermobarograms obtained for 16FBTFO$_1$M$_7$ showing; a) and b) the mesomorphic polymorphism under low pressure c) the polymorphism under high pressure

change of slope, due to the different values of the thermal expansion α_P and of the isothermal compressibility χ_T on both side of the transition; this is clearly a second order transition. The existence of a very small pressure increment associated to a TGB$_A$–N^* allows to qualify this transition as a weakly first order transition. A very clear pressure increment (about 10 MPa) which is characteristic of first order transition, is associated to a N^*–I transition; the slope of the N^*–I transition line (equilibrium curve) is about 2.2 MPa K^{-1} . Thermobarogram of Fig. 2c exhibits at low temperature an abrupt change on slope, which occurs at 336 K, followed by a strong increase on pressure (about 30 MPa) associated to the melting (K–S_C^* transition); the slope of the equilibrium curve (biphasic portion of the thermobarogram corresponding to the Clapeyron curve [18]) at K–S_C^* transition is 4.6 MPa K^{-1}. As shown by Fig. 2c, the five stable phases observed under atmospheric pressure are always detected under high pressure.

For n=18, thermobarograms obtained under relatively low pressure (Fig. 3a) exhibit always the S_C^*–TGB$_A$–I phase sequence. The associated transi-

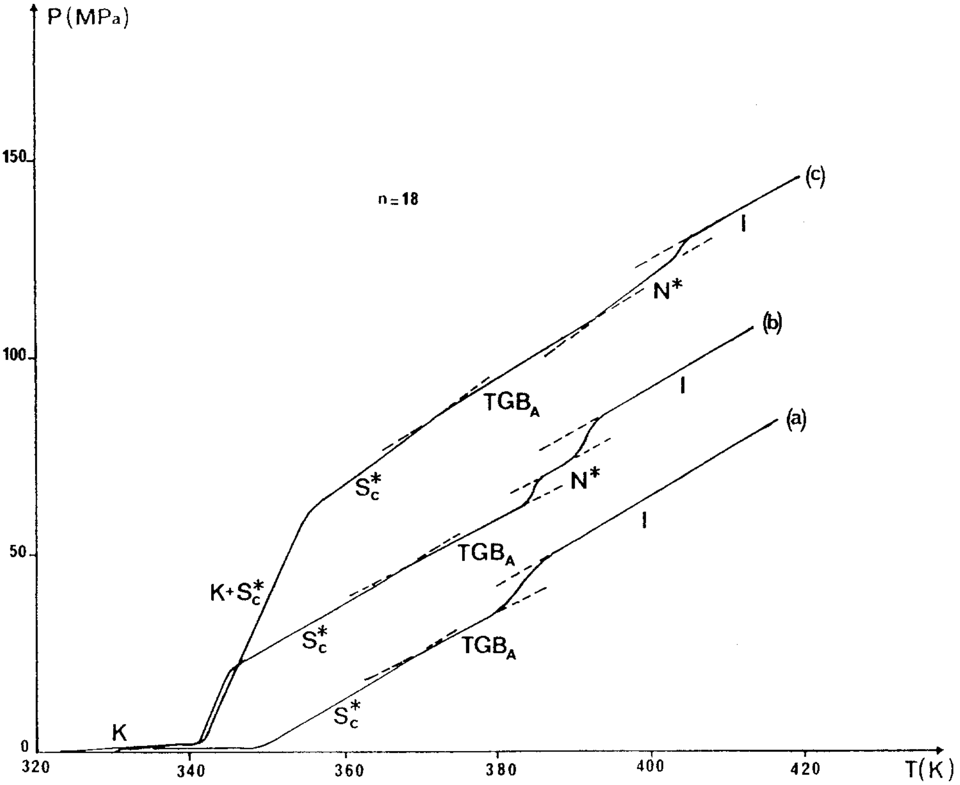


Fig. 3 Examples of thermobarograms obtained for 18FBTFO$_1$M$_7$ showing: a) the mesomorphic polymorphism below the TGB$_A$–N^*–I triple point b) and c) the mesomorphic polymorphism above the TGB$_A$–N^*–I triple point

tions S_C^*–TGB$_A$ and TGB$_A$–I are respectively second order and first order; the pressure increment corresponding to the clarification (biphasic portion TGB$_A$+I of thermobarogram) is about 13 MPa. Thermobarograms presented in Figs. 3b and c give the polymorphism under high pressure. The pressure change observed for the melting is about 68 MPa. Four fluid stable phases are then detected on Figs. 3b and c pointing out an intermediate phase is induced by pressure between TGB$_A$ and I phases. Then, according to the phase sequences observed under atmospheric pressure for lower homologous [7], the pressure induced mesophase can be identified as a N^* phase. Thus, two transitions are associated to that induced mesophase. The N^*–I transition with 10 MPa pressure increment is clearly first order. The TGB$_A$–N^* transition is observed as first order under intermediate pressure (only a small pressure change is detected on Fig. 3b); it becomes practically second order under higher pressure (Fig. 3c), where only a change of slope is observed. Whatever the pressure, the S_C^*–TGB$_A$ transition is always second order.

Discussion

Figure 4 and 5 gives the resulting pressure–temperature phase diagram for $n=16$ and $n=18$ respectively. On these diagrams, transitions are reported as full lines for equilibrium curves (first order transitions), plotted by using mean values from several thermobarograms for the Clapeyron slopes and for the transition temperatures at atmospheric pressure. Dashed lines give second order or very weakly first order transitions obtained by using the transition temperatures under different pressures (measured at the slope change) given by several thermobarograms. Most of the second order transitions (or for weakly first order) are difficult to detect because of the close values of α_P/χ_T ratios for the two successive phases. So, the T and P values at the characteristic point are determined with a large uncertainty. Thus, for second order transition, the estimated precision on the temperature values is lower than 2 K for pressure lower than 40 MPa and is about 3 K for higher pressure. Figures 4 and 5 show that the temperature stability domain of S_C^* decreases with increasing pressure whereas

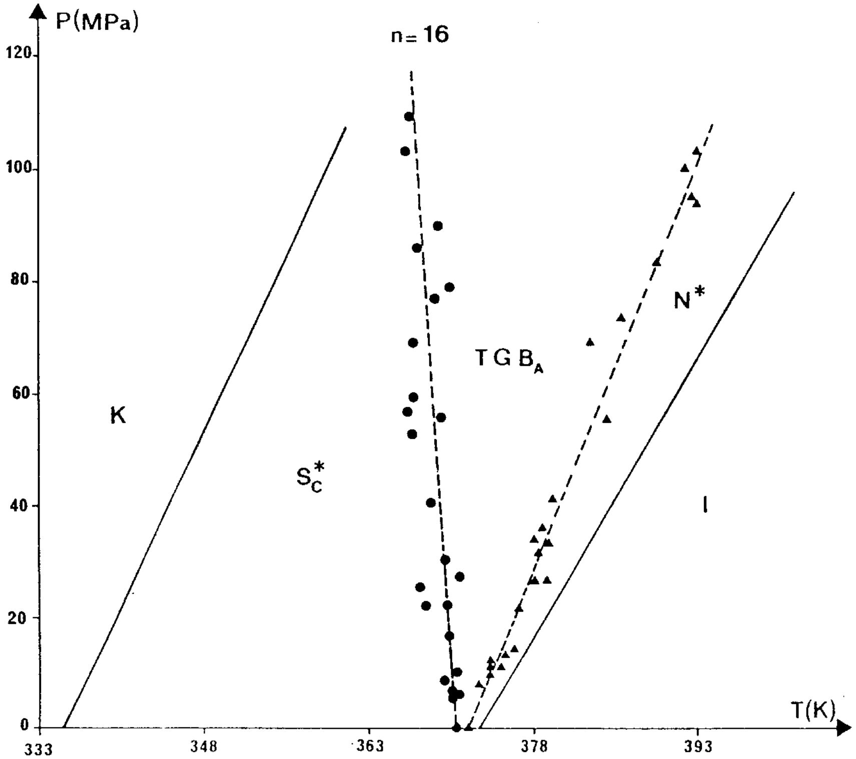


Fig. 4 Pressure–temperature phase diagram for $16FBTFO_1M_7$: full lines: first order phase transitions; dashed lines: weakly first order or second order phase transitions

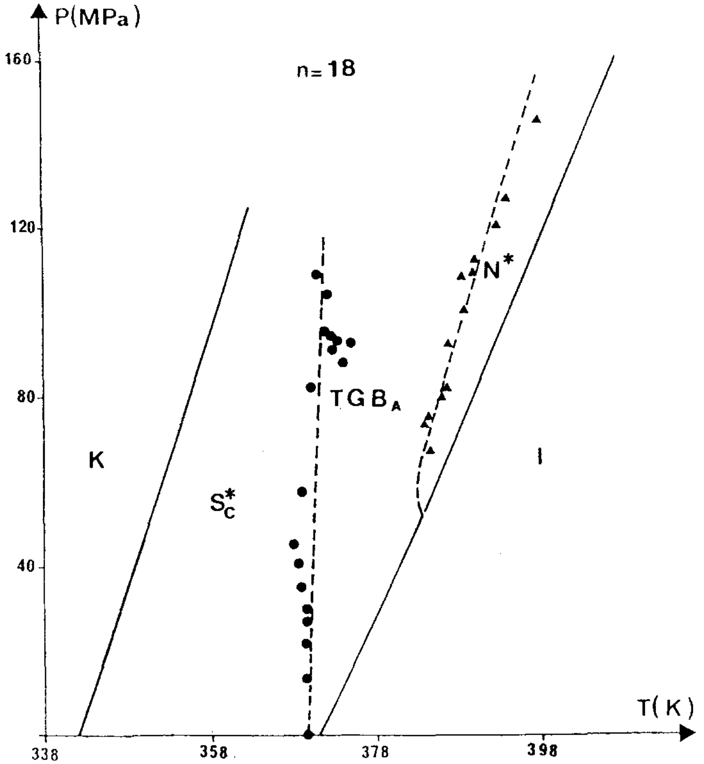


Fig. 5 Pressure–temperature phase diagram for 18FBTFO$_1$M$_7$: full lines: first order phase transitions; dashed lines: weakly first order or second order phase transitions

the N^* and TGB$_A$ phases are stabilized with increasing pressure. The behaviour of TGB$_A$ phase under pressure is in agreement with results recently obtained [10] on $n=10$ and $n=11$ homologous. For $n=18$, the boundary lines associated to N^*, TGB$_A$ and I phases intercept at (50±1) MPa and (383±3) K; taking account both TGB$_A$–I and N^*–I transitions are always first order whatever the pressure and TGB$_A$–N^* transition is first order under intermediate pressure, the boundary line intersection is not a multicritical point but simply a triple point. It will be noted here the negative slope of S_C^*–TGB$_A$ boundary line for $n=16$. The same behaviour have already been observed in P–T phase diagram of $n=11$ [10] and also for P–T phase diagrams exhibiting reentrant phenomena [13, 19]. Assuming the slope of S_C^*–TGB$_A$ second order boundary line is given by Ehrenfest relation [20] $\mathrm{d}P/\mathrm{d}T=\Delta\alpha/\Delta\chi$, where $\Delta\alpha$ and $\Delta\chi$ are the isobaric thermal expansion and isothermal compressibility changes at phase transition, the negative slope implies that either $\Delta\alpha$ or $\Delta\chi$ is negative. Other experiments are required for giving explanations of this behaviour.

Conclusion

High pressure measurements have been performed, by thermobarometric analysis on the two homologous 16 and 18 of the FBTFO$_1$M$_7$ chiral chemical series. The pressure–temperature phase diagrams have been determined for both compounds and show that the TGB$_A$ phase is stabilized by increasing pressure. The appearance, under high pressure, of the cholesteric phase in the P–T phase diagram for $n=18$ leads to the observation of a TGB$_A$–N^*–I triple point; the TGB$_A$–N^* transition becomes second order under high pressure. For both compounds, transitions under pressure are always second order for S_C^*–TGB$_A$ and first order (or weakly first order) for the other.

References

1 S. R. Renn and T. C. Lubensky, Phys. Rev. A, 38 (1988) 2132.
2 S. R. Renn, Phys. Rev. A, 45 (1992) 953.
3 J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, Nature, 337 (1989) 449.
4 A. Bouchta, H. T. Nguyen, M. F. Achard, F. Hardouin, C. Destrade, R. J. Twieg, A. Maaroufi and N. Isaert, Liq. Cryst., 12 (1992) 575.
5 H. T. Nguyen, A. Bouchta, L. Navailles, P. Barois, N. Isaert, R. J. Twieg, A. Maaroufi and C. Destrade, J. de Phys. II France, 2 (1992) 1889.
6 J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, J. Am. Chem. Soc., 111 (1989) 8119.
7 H. T. Nguyen, R. J. Twieg, M. F. Nabor, N. Isaert and C. Destrade, Ferroelectrics, 121 (1991) 187.
8 A. J. Slaney and J. W. Goodby, Liq. Cryst., 9 (1991) 849.
9 O. D. Lavrentovich, Yu. A. Nastishin, V. I. Kulishov, Yu. S. Narkevitch, A. S. Tolochko and S. Shiyanovskii, Europhys. Lett., 13 (1990) 313.
10 A. Anakkar, A. Daoudi, J.-M. Buisine, N. Isaert, T. Delattre, H. T. Nguyen, C. Destrade, J. Thermal Anal., 41 (1994) 1001.
11 The TGB$_C$ phase is not mentioned in Ref. [4]; it has very recently observed by thermal microscopy for $n=12$, 13 and 14 homologous by N. Isaert and F. Bougrioua.
12 H. T. Nguyen, J. Chim. Phys., 80 (1983) 83.
13 V. N. Raja, B. R. Ratna, R. Shashidhar, G. Heppke, Ch. Bahr, J. F. Marco, J. O. Indekeu and A. Nihat Berker, Phys. Rev. A, 39 (1989) 4341.
14 J.-M. Buisine and B. Soulestin, Rev. Phys. App., 22 (1987) 1211.
15 J.-M. Buisine, B. Soulestin and J. Billard, Mol. Cryst. Liq. Cryst., 97 (1983) 397.
16 J.-M. Buisine, B. Soulestin and J. Billard, Mol. Cryst. Liq. Cryst., 91 (1983) 115.
17 J.-M. Buisine, Mol. Cryst. Liq. Cryst., 109 (1984) 143.
18 P. Clapeyron, J. Ec. Polytech., 14 (1834) 153.
19 A. N. Kalkura, R. Shashidhar and N. Subramanya Raj URS, J. de Phy., 44 (1983) 51.
20 P. Ehrenfest, Leiden. Comm. Supp., 75B (1933) 8.