

Experimental observation of multicritical behaviors in pressure-temperature diagrams of pure compounds with twist grain boundary phases

A. Anakkar,^{1,*} N. Isaert,¹ M. Ismaili,¹ J.-M. Buisine,² and H. T. Nguyen³

¹Laboratoire de Dynamique et Structure des Matériaux Moléculaires, URA CNRS No. 801, Equipe de Physique des Stases Anisotropes, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cédex, France

²Laboratoire de Dynamique et Structure des Matériaux Moléculaires, URA CNRS No. 801, Equipe de Thermophysique de la Matière Condensée, Université du Littoral, Quai Freycinet 1, Boîte Postale 5526, F59379 Dunkerque, France

³Centre de Recherche Paul Pascal, Avenue A. Schweitzer, 33600 Pessac, France

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In order to study critical behaviors of pure compounds anticipated by Renn and Lubensky's theoretical calculations, high-pressure experiments have been performed on six tolan series homologous to the 3-fluoro-4-[(*R*) or (*S*)-methylheptyloxy]-4'-(4"-alkoxy-2",3"-difluorobenzoyloxy), which exhibit the twist grain boundary (TGB_A and TGB_C) mesophases. Measurements were carried out by thermobarometric analysis. Six pressure-temperature phase diagrams are determined. The studies establish the existence of multicritical points twisted-smectic-*C* (S_C^*)- TGB_C - TGB_A , TGB_C - TGB_A -cholesteric nematic (N^*) and S_C^* - TGB_C - N^* for single component systems in pressure-temperature (P - T) phase diagrams. Our results also show that a pressure increase has the same effect on the (P - T) phase diagrams as a decreasing number of carbon atoms in the aliphatic chain; then pressure change can have the same effects on intermolecular interactions as those observed when shortening the molecular length. The existence of transition lines with negative slope values was also found. The experimental results are in qualitative agreement with the model proposed by Renn and Lubensky. [S1063-651X(99)07107-X]

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I. INTRODUCTION

Many publications have shown that liquid crystals are materials especially well fitted to theoretical and experimental studies of critical phenomena. The evidence of such thermodynamic behavior is most often improved in temperature-concentration (T - X) phase diagrams [1–3], and this is seldom shown in pressure-temperature (P - T) phase diagrams [3–5], especially for multicritical points. In this last case, nematic-smectic *A*-smectic *C* (NAC for short) for achiral molecules [6,7] and cholesteric smectic *A*-twisted smectic *C*, denoted (NAC)* for chiral molecule [8] multicritical points have been observed in P - T phase diagrams.

In 1992, Renn and Lubensky [9–12] calculated three phase diagrams showing the new twist grain boundary (TGB) smectic mesophases (TGB_A , TGB_C , and TGB_C^*) in which several multicritical points are displayed. The phase diagram obtained by Renn and Lubensky and given in Fig. 1 contains two of these mesophases (TGB_A and TGB_C) and five multicritical points denoted B_1 , B_2 , B_3 , L , and CEP.

It is well known that, for chemical series, systematic variation of aliphatic chain lengths considerably influences the thermal stability of mesophases: phase sequences change versus the number of carbons in the aliphatic chain [13–16] and sometimes an odd-even effect can be observed [17–19].

The binary mixture of two compounds having different or the same phase sequences can exhibit a large number and a great variety of new phenomena: induced mesophases [20–

24], reentrant mesophases [2,3,21–26], a twist inversion in cholesteric mesophase [21], etc. Thus, experiments under atmospheric pressure performed on mixtures have shown the effect of composition on the stability of TGB mesophases [12–15,27]. These studies have led to the observation of all the multicritical points involving TGB_A and TGB_C mesophases [12–14,21,24,27–30] predicted by Renn and Lubensky's theory.

At the same time, all these interesting phenomena can also be observed by increasing pressure. As a matter of fact, some mesophases can appear or disappear as a function of pressure. Thus, it is well known that it leads to the observation in the pressure-temperature phase diagram of triple and/or multicritical points which are due to pressure-bounded and/or pressure-induced mesomorphism [31–33].

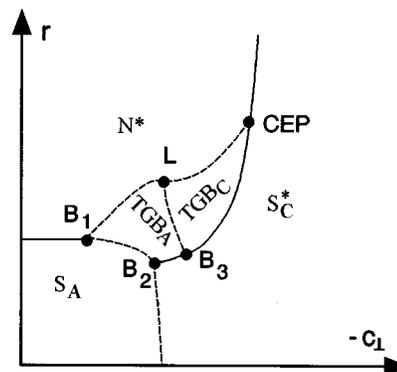


FIG. 1. Theoretical phase diagram predicted by Renn and Lubensky (reproduced from Ref. [12]); solid lines are associated with first-order phase transitions and dashed lines with weakly first-order or second-order phase transitions.

*Author to whom correspondence should be addressed. Electronic address: anakkar@lip5rx.univ-lille1.fr

TABLE I. Experimental data for the phases and transitions under atmospheric pressure: Transition temperature T and enthalpy changes ΔH , note that the isotropic phase exists for all values of n .

n	Cr		S_C^*		TGB_C		S_A		TGB_A		N^*		BP	
	T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)
9	336.2	35	361.3			a	372.3	0.56 ^b	376.7		387.4		387.5	0.99 ^c
10	332.2	34.4	371.5			a		a	378.9	0.56 ^b	387.6		388.8	1.17 ^c
11	319.5	44.8	373.7		374.4	0.11 ^b		a	377.3		385.0		385.8	1.2 ^c
12	309.9	27.7	375.7		376.1	1.7 ^b		a		a	383.6		384.8	1.19 ^c
14	334.3	48.29	377.4	0.69		a		a		a	380.8		381.0	1.89 ^c
16	330.8	41.32	377.7	0.9		a		a		a	379.4		379.6	2.1 ^c

^aThe phase does not exist for the compound.

^bThe sum of two transitions: S_A - TGB_A and TGB_A - N^* or S_C^* - TGB_A and TGB_A - N^* or S_C^* - TGB_C and TGB_C - TGB_A or S_C^* - TGB_C and TGB_C - N^* .

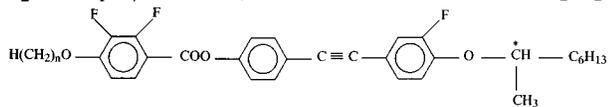
^cThe sum of two transitions: N^* -BP and BP-I.

However, only a few high-pressure studies of TGB mesophases have been carried out. TGB_A - N^* -I [34] and S_C^* - TGB_A -I [33] triple points in pure compounds have been obtained under pressure. Until today, only B_1 [32] and B_2 [31,32] were observed in pressure-temperature phase diagrams for single component systems. Moreover, multicritical points with TGB_C mesophase have not yet been observed in pure compounds.

In order to give experimental evidence of new multicritical points in pure ferroelectric liquid crystals (FLC), in this paper we will first report thermobarometric measurements performed especially on compounds which display TGB_A and TGB_C mesophases. P - T phase diagrams are interpreted and a qualitative comparison with Renn and Lumbensky's theoretical phase diagram is presented. This work is part of a more general study of the effect of pressure on phase sequences, on the thermal stability of mesophases, and on the nature of a transition for new FLC compounds involving TGB mesophases.

II. COMPOUNDS

Our present studies relate to the homologous series with chiral molecules: 3-fluoro-4-[(*R*) or (*S*)-methylheptyloxy]-4'-[4''-alkoxy-2'',3''-difluorobenzoyloxy] tolan ($nF_2BTFO_1M_7$ for short) whose chemical formula is [13]



Six chiral liquid crystal compounds are chosen. Phase identifications and transition temperatures under atmospheric pressure were determined by both thermal microscopy and differential scanning calorimetry (DSC) [13,35,36]. This homologous series is very interesting because of its rich mesomorphism involving TGB mesophases, which are sensitive to changes in the alkoxy chain length. The phase sequences and transition temperatures and enthalpies, at atmospheric pressure, are presented in Table I.

All members of the series display the following mesophases between the crystalline (Cr) and isotropic (*I*) phases: twisted smectic C (S_C^*), cholesteric (N^*), and blue phase (BP). The S_A mesophase exists for $n=9$ and disap-

pears in long lateral chains ($n \geq 10$). The TGB_A temperature range is between 3 and 7.4 °C, and it disappears for $n \geq 12$. The TGB_C mesophase exists only for $n=11$ and 12 compounds and displays a very narrow temperature range (less than 0.7 °C). It is interesting to note that the enthalpy values for transitions between mesophases are very small. Moreover, these transitions are weakly first-order or second-order ones.

III. RESULTS

Studies of phase transitions were performed under pressure by thermobarometric analysis (TBA) using an automated metabolemeter (SCERES, MAB 02 A 20). Measurements consisted in recording, versus temperature, the pressure of a small sample (about 10 mg) enclosed in a metallic cell. The details of this technique and interpretations of thermobarograms have been sufficiently described elsewhere [37–40] in the classical liquid crystalline systems without TGB mesophases, and more recently, in ferroelectric liquid crystals involving TGB_A mesophase in Refs. [31, 34].

Measurements were performed for temperatures between

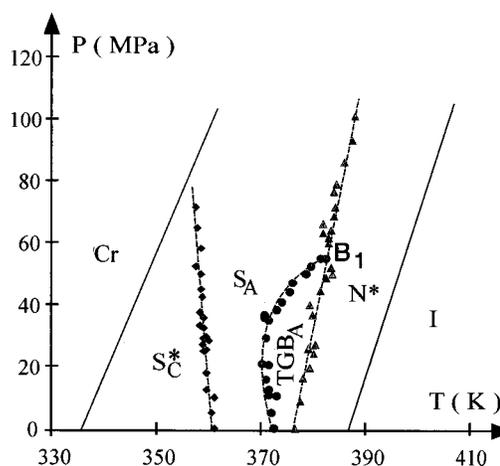


FIG. 2. Pressure-temperature phase diagram for $9F_2BTFO_1M_7$. The disappearance of TGB_A mesophase under pressure leads to the S_A - TGB_A - N^* multicritical point noted B_1 .

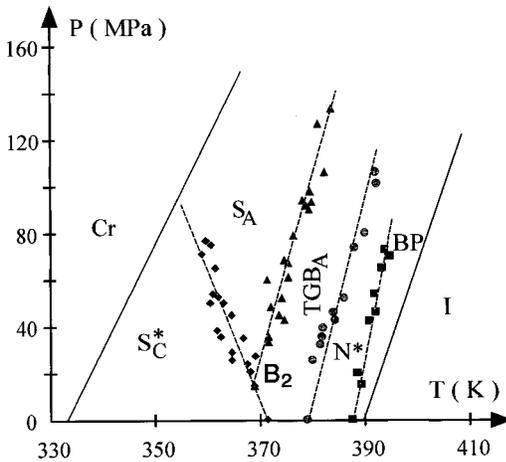


FIG. 3. Pressure-temperature phase diagram for $10F_2BTFO_1M_7$. The pressure-induced mesophase is an S_A one. Then, this diagram shows the multicritical point $S_C^*-S_A-TGB_A$ noted B_2 .

300 and 500 K and for pressures up to 160 MPa. Thermobarograms were plotted with a 0.5 deg min^{-1} heating rate. The exploitation of thermobarogram networks including several heating runs plotted for different initial conditions led to the pressure-temperature phase diagrams presented in Figs. 2–7. In these diagrams, transitions are reported as solid lines for equilibrium curves (first-order transitions). Dashed lines correspond to second-order or weakly first-order transitions. Some mesophases can appear or disappear as a function of pressure; in both cases, such behavior led to triple and/or multicritical points.

Some pressure-temperature domains of phases (crystalline and isotropic) or mesophases were easily identified from phase sequences under atmospheric pressure. Nevertheless, the identification of pressure-induced mesophases requires argumentation. These results will be discussed in detail below.

IV. DISCUSSION

A. Position of the different compounds in Renn and Lubensky's diagram

The phase sequences, under atmospheric pressure, of the six homologous series can be represented by straight lines in

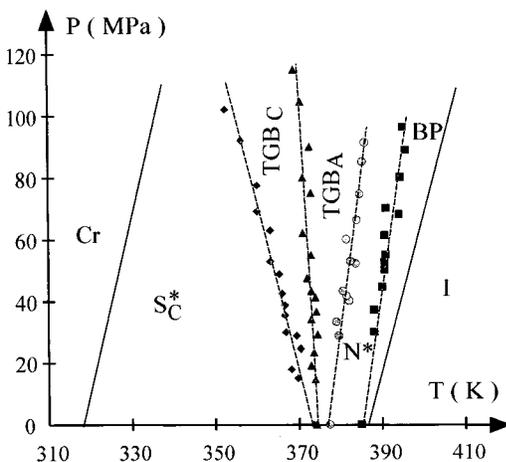


FIG. 4. Pressure-temperature phase diagram for $11F_2BTFO_1M_7$.

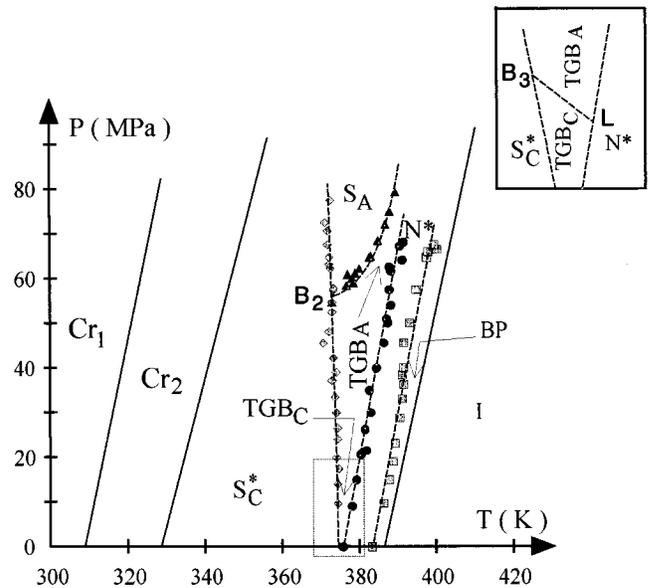


FIG. 5. Pressure-temperature phase diagram for $12F_2BTFO_1M_7$. Two mesophases are induced: TGB_C and TGB_A ; three multicritical points are present: B_2 , B_3 , and L (inset).

Renn and Lubensky's diagram as is shown in Fig. 8. For example, the straight line showing the phase sequence of $n=9$ is located between points B_1 and B_2 ; for $n=10$ it is between B_2 and B_3 , etc. The temperature (T) axis is obviously defined by the transition from an ordered phase to a disordered one. The pressure (P) axis was chosen in order to be consistent with our experimental results. This choice will be justified in the next discussion.

B. Singular points and melting curve in the (P - T) phase diagrams

$$n=9$$

For the $n=9$ compound, the phase sequence, under atmospheric pressure, is $Cr-S_C^*-S_A-TGB_A-N^*-BP-I$. In the P - T phase diagram (Fig. 2), the TGB_A temperature range versus pressure first increases slightly, then rises to a maximum,

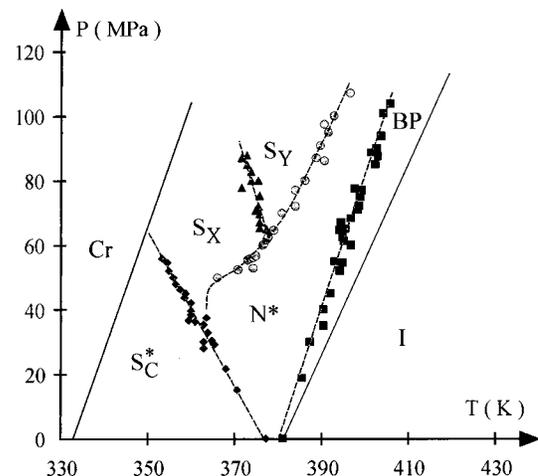


FIG. 6. Pressure-temperature phase diagram for $14F_2BTFO_1M_7$. $S_X=TGB_C$ and $S_Y=TGB_A$. Two multicritical points are present: CEP and L .

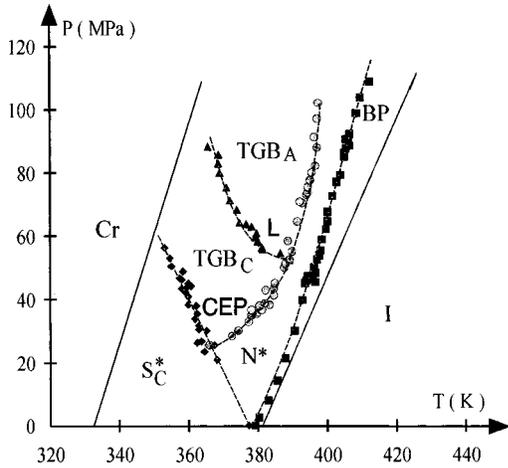


FIG. 7. Pressure-temperature phase diagram for $16F_2BTFO_1M_7$. Like $14F_2BTFO_1M_7$, this diagram presents clearly the CEP and L multicritical points.

and, finally, decreases and disappears to give rise to multicritical point S_A - TGB_A - N^* denoted B_1 in Renn and Lubensky's phase diagram. Thus, it appears clearly that the disappearance of the TGB_A mesophase under pressure justifies our choice for the position of the P axis (Fig. 8) in Renn and Lubensky's diagram.

The temperature range of the S_C^* mesophase vanishes when pressure is increased. Therefore, there is a Cr - S_C^* - S_A singular point. In thermobarograms, no pressure increment is detected in the S_C^* - S_A transition, which can be interpreted as a second-order or weakly first-order transition. Because the melting (Cr - S_C^* for lower pressure, Cr - S_A for higher pressure) has to be of first order, point Cr - S_C^* - S_A can be a triple point if the S_C^* - S_A transition becomes (weakly) first order in the vicinity of this point. On the contrary, if the S_C^* - S_A transition remains second order up to the intersection point, this point is a multicritical one. The resolution of our equipment has not allowed us to solve this problem and to determine the topology of this singular point.

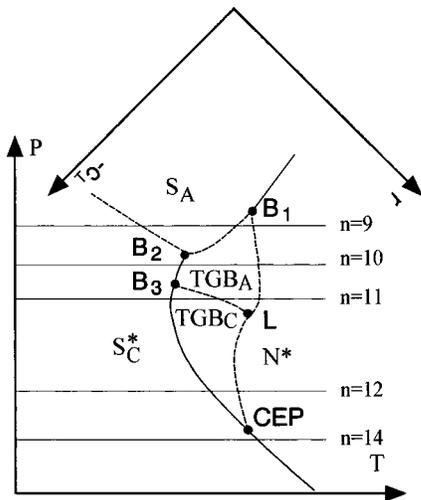


FIG. 8. Theoretical phase diagram predicted by Renn and Lubensky [12] in the pressure and temperature axes. Phase sequences under atmospheric pressure for all the members of the series.

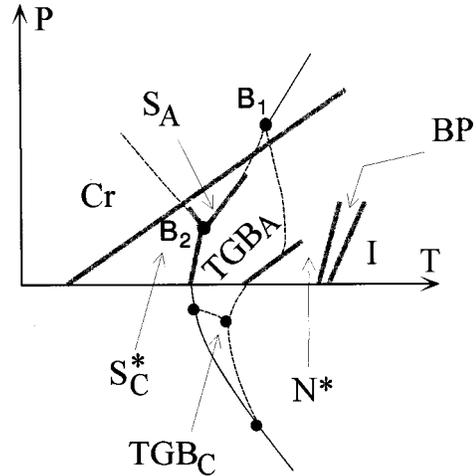


FIG. 9. Experimental transition lines of $10F_2BTFO_1M_7$ (thick lines) in Renn and Lubensky's phase diagram.

The thermal stability range for the BP mesophase, under atmospheric pressure, is about or less than $0.1^\circ C$, and is too small to be clearly separated.

The transition line form of S_A - TGB_A suggests the existence of a reentrant phenomenon. In fact, at constant temperature between 370.3 and 372.3 K, the following phase sequence can be observed versus pressure: S_A - TGB_A - S_A .

$n = 10$

For the $n = 10$ compound, the sequence under atmospheric pressure is Cr - S_C^* - TGB_A - N^* - BP - I . A high-pressure branching of the S_C^* - TGB_A line gives way to two transition lines (Fig. 3). Thus, a new mesophase is induced under pressure. By comparison with Renn and Lubensky's diagram (Fig. 8), this mesophase can be identified as an S_A one. Then, point S_C^* - S_A - TGB_A corresponds to a multicritical point B_2 . The induced mesophase, between S_C^* and TGB_A , might be a TGB_C one. This possibility may be excluded because it is at variance with the choice of the P axis position (Fig. 8), which has been confirmed by the $n = 9$ compound. The disappearance of the TGB_A mesophase corresponding to the B_1 point is not experimentally observed for this compound. Point B_1 exists perhaps at too high a pressure to be detected with our equipment; it can also be located above the melting curve as shown in Fig. 9.

The S_C^* mesophase disappears under pressure in a singular point Cr - S_C^* - S_A ; for the reasons such as those evoked for the $n = 9$ compound, the Cr - S_C^* - S_A can be a triple or multicritical point.

$n = 11$

For $n = 11$, two TGB mesophases exist under atmospheric pressure. The P - T phase diagram (Fig. 4) shows that their domains of stability increase under pressure. The extrapolation of the S_C^* - TGB_C line transition leads to the prediction of a singular point Cr - S_C^* - TGB_C for pressures superior to 120 MPa. Above this singular point, at constant pressure, upon heating in the Cr phase, it undergoes a direct transition into the TGB_C mesophase. The TGB_C - TGB_A transition line can also intersect the melting curve but for high-pressure values.

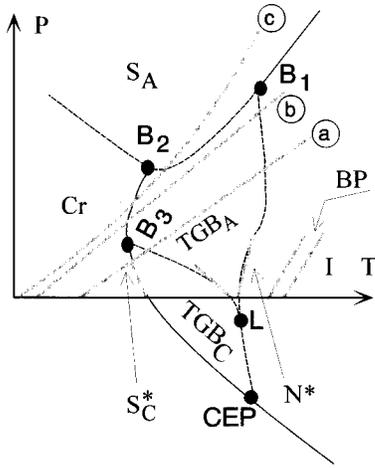


FIG. 10. Experimental transition lines of $11F_2BTFO_1M_7$ (thick lines) in Renn and Lubensky's phase diagram.

Then, we should have the Cr - TGB_C - TGB_A singular point and above it there should be a direct transition from a crystalline phase Cr to the TGB_A mesophase. Such Cr - TGB_A or Cr - TGB_C transitions, which have never been observed in our compounds under atmospheric pressure, have been obtained in other types of compounds [41,42].

Another hypothesis could be the existence of a TGB_C bounded mesophase between S_C^* and TGB_A mesophases. Thus, we should have an S_C^* - TGB_A transition line that should intersect the melting curve. Then, there should be two singular points; the first one should be Cr - S_C^* - TGB_A and the second one S_C^* - TGB_C - TGB_A , denoted B_3 in Renn and Lubensky's phase diagram. The uncertainty concerns the position of the melting curve which can be below point B_3 (Fig. 10, line *a*) or above point B_3 (Fig. 10, lines *b* and *c*). In the first case (*a*), both points B_2 and B_3 are in a metastable area corresponding to the crystalline phase. In cases (*b*) and (*c*), point B_2 is in a metastable region. Point B_1 could be obtained if the slope that characterizes the melting curve has the adequate value in Renn and Lubensky's diagram; an example is given with curve (*c*). However, it is not possible with our P - T equipment to have access to these metastable states experimentally.

$n = 12$

First of all, under atmospheric pressure the following phase sequence Cr_1 - Cr_2 - S_C^* - TGB_C - N^* - BP - I for the $n = 12$ compound does not display the S_A and TGB_A mesophases. On the other hand, the P - T phase diagram (Fig. 5) shows that the stability range of S_C^* decreases slowly when pressure increases. Eventually, it disappears in the singular point deduced by extrapolation for about 130 MPa.

Of course, the appearance of a mesophase that leads to a singular point, clearly experimentally identified under 55 MPa, is the most important thing. The identification of such an induced mesophase is not easy.

Let us consider the effect of heating from the S_C^* mesophase to the N^* one, at constant pressure, above and below the singular point corresponding to 55 MPa. Above this singular point, if we exclude improbable phase sequences such as S_C^* - TGB_A - TGB_C - N^* (inverted sequence for the tilt A/C),

S_C^* - TGB_A - S_A - N^* , and S_C^* - TGB_C - S_A - N^* (inverted sequence for the TGB twist), there are two solutions left: S_C^* - TGB_C - TGB_A - N^* and S_C^* - S_A - TGB_A - N^* phase sequences. This means that the TGB_A mesophase is to appear under pressure and the TGB_C mesophase will display an enclosed area. Then, somewhere below the singular point, we should get a TGB_C - TGB_A transition line in the P - T diagram, as shown in the top right-hand corner in Fig. 5.

For the first solution, the P - T phase diagram has two TGB_C domains and there may be two points B_2 . This is more unlikely and disagrees with Renn and Lubensky's theoretical phase diagram.

The only reasonable solution consists in deducing that the pressure-induced mesophase above the 55 MPa singular point is an S_A one. It corresponds to the following phase sequence S_C^* - S_A - TGB_A - N^* .

Some other arguments bear out this interpretation. Indeed, dielectric measurements at atmospheric pressure in the $n = 12$ compound [43] show an important soft mode associated with the TGB_C - N^* transition. This behavior is in agreement with a typical A mesophase in the vicinity of atmospheric pressure (here TGB_A mesophase). So, the TGB_A mesophase must appear under pressure for values very close to atmospheric pressure and the TGB_C mesophase disappears at low pressure. In addition, the TGB_C thermal stability range determined by optical and DSC measurements under atmospheric pressure is less than $0.4^\circ C$. Then, its P - T domain would be very weak. That is why thermobarograms plotted for relatively weak values of the pressure did not allow us to obtain separately TGB_C and TGB_A mesophases using the present P - T equipment.

As a result, four singular points can be deduced: a singular point Cr_2 - S_C^* - S_A (obtained by extrapolation) and three multicritical points S_C^* - S_A - TGB_A (observed experimentally), S_C^* - TGB_C - TGB_A , and TGB_C - TGB_A - N^* (reasoned argument) denoted B_2 , B_3 , and L in Renn and Lubensky's phase diagram.

Let us see what happens with the phase sequences and how their positions are related to the last three multicritical points. As before, we assume that the temperature increases from the S_C^* mesophase to the N^* one at different constant pressures.

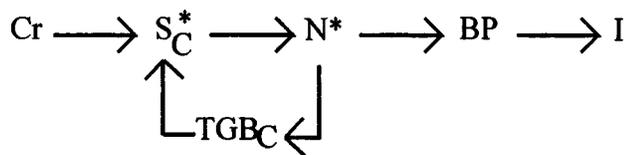
Up to point L , the phase sequence is S_C^* - TGB_C - N^* . Between L and B_3 , there is an S_C^* - TGB_C - TGB_A - N^* phase sequence. From B_3 to B_2 , we have an S_C^* - TGB_A - N^* one. Above point B_2 , the S_C^* - S_A - TGB_A - N^* sequence occurs. These phase sequences are ordinary ones: all have been observed, under atmospheric pressure, on other compounds elsewhere [14,15,44-46].

To sum up, the built-up analysis along the arguments has more and more confirmed our choice of the pressure and temperature axes in Renn and Lubensky's phase diagram.

$n = 14$

For the $n = 14$ compound, initial studies [13] performed under atmospheric pressure, i.e., DSC measurements and optical texture observations, have not revealed TGB_A and TGB_C mesophases. Our additional optical observations have shown the existence of a monotropic TGB_C mesophase on a

very narrow temperature range. Then the phase sequence under atmospheric pressure is



The P - T phase diagram (Fig. 6) shows a bounded S_C^* mesophase and two pressure-induced mesophases which are denoted S_X and S_Y . According to what was said above for $n=12$, there remain only two possibilities for the mesophases that appear under pressure: $S_X=S_A$ and $S_Y=TGB_A$ or $S_X=TGB_C$ and $S_Y=TGB_A$.

The first one, $S_X=S_A$ and $S_Y=TGB_A$, requires the disappearance of the TGB_C mesophase first and afterwards there must be three multicritical points: S_C^* - TGB_C - N^* (denoted CEP), S_A - TGB_A - N^* (point B_1), and finally S_C^* - S_A - N^* , which may be near atmospheric pressure. The last singular point, though it is well known, according to the theoretical phase diagrams that have been established by Renn and Lubensky, cannot occur when there are some TGB mesophases. Moreover, dielectric measurements were carried out for the $n=14$ compound [43]. The soft mode observed for $n=14$ is half as important as for $n=12$. Thus, a type- A mesophase (S_A or TGB_A) has to be far from atmospheric pressure. So, this solution does not seem to be suitable.

Therefore, the induced mesophase S_X is the TGB_C one; it is monotropic under atmospheric pressure and becomes enantropic when pressure is increased. Taking into account that for low pressures the TGB_C mesophase is monotropic and its temperature range is very narrow, the coordinates of point S_C^* - TGB_C - N^* (denoted CEP in Renn and Lubensky's diagram) are not very accurate.

So the high-pressure-induced mesophase S_Y is a TGB_A one, which leads to a multicritical point TGB_C - TGB_A - N^* (denoted L in Renn and Lubensky's diagram).

$n=16$

A very similar phase diagram (Fig. 7) has been found for the last compound $n=16$. This diagram clearly shows two pressure-induced mesophases. Following the interpretation given for $n=14$, they were also identified as TGB_C and TGB_A . However, the CEP multicritical point was found with more accuracy than for $n=14$, because the TGB_C was not detected as monotropic under atmospheric pressure. Then, in the $n=14$ and 16 (P - T) phase diagrams, we have four singular points: CEP, L , Cr - S_C^* - TGB_C and Cr - TGB_C - TGB_A (the last point was determined by extrapolation). Thus, when temperature is increased at some constant pressures, the crystalline phase Cr can directly pass to TGB_A or TGB_C mesophase. In this case, using the arguments which are completely similar to those given for $n=10$ and 11 compounds, the melting curve is such that it masks points B_3 and B_2 . Concerning point B_1 , it can also be masked or may be found for pressure superior to 120 MPa.

Once again, both phase diagrams confirm the choice of the P and T axes in Renn and Lubensky's theoretical phase diagram.

C. Relationship between the pressure (P) and the aliphatic chain (n)

Figure 8 displays Renn and Lubensky's theoretical diagram with the new experimental axes pressure and temperature. For each compound we have reported, the T axis corresponds to atmospheric pressure. If we superpose the experimental diagrams on the theoretical one, we will obtain interesting behaviors. One is as follows: according to this figure, for $n=14$ and 16, the increase of pressure first has to induce the TGB_C mesophase and then the TGB_A one. Actually two mesophases appear in each experimental phase diagram of both $n=14$ and 16 compounds. A very similar analysis can be carried out for the other compounds. Then, it becomes clear that a pressure increase (respectively a decrease) has the same effect on the P - T phase diagrams as a decrease (respectively an increase) in the number of carbon atoms in the aliphatic chain. A similar result has also been found in other series by Spratte and Schneider [47,48].

D. Concerning the stability domains of phases

For all the studied substances, the stability domains of both BP and N^* mesophases often increase with pressure. When the S_A mesophase exists, it is also stabilized by pressure. However, for all the compounds of the series, the temperature range of the S_C^* regularly decreases when pressure is increased and finally vanishes at high pressure leading to a bounded S_C^* mesophase. Then two types of singular points appear on the P - T diagrams: Cr - S_C^* - S_A or Cr - S_C^* - TGB_C . Moreover, our experimental results show that the temperature ranges of TGB_A and TGB_C mesophases can disappear when increasing the pressure, but can also increase first, then rise to a maximum, and finally completely disappear at high pressure. For most of the transformations, the transition temperature varies in the same way as pressure. However, it must be noted that the slopes of the S_C^* - S_A , S_C^* - TGB_A , S_C^* - TGB_C , and TGB_C - TGB_A transitions are negative, showing that, in these cases, the transition temperature decreases when pressure is increased. Detailed discussion of this behavior is presented in Ref. [32].

E. About the chiral line liquid

This homologous series has also been studied by Navailles *et al.* [49]. Using high-resolution calorimetry, under atmospheric pressure, they observed new phenomena. It is useful to note that the quantity (typically 50 mg) used by them is five times larger than that reported in this paper, and their scan rates are much smaller than ours.

As can be seen in thermograms of DSC experiments according to the previous studies of Nguyen *et al.* [13], the evolution from TGB_A mesophase to N^* is characterized by a wide peak in the $n=10$ and 11 compounds and for $n=12$ the N^* basic line is not a straight line.

For $n=10$, in the TGB_A domain that was determined by DSC, Navailles *et al.* detected a very weak enthalpy variation which was interpreted as the melting of the screw dislocation network. Then, in the previous TGB_A area, there are two mesophases: the TGB_A one is found in the low-temperature range, and a new mesophase, with a short-range TGB_A structure in which screw dislocations are disordered,

and which is called chiral line liquid, noted N_L^* [49,50], is found in the high-temperature range.

As N_L^* and N^* are not thermodynamically distinct mesophases, the enthalpy variation detected from TGB_A to N_L^* is not interpreted as a phase transition but rather as a locus of maximum heat capacity [49,50].

For $n=12$, in the previous N^* domain [13], high-resolution calorimetry also revealed a weak maximum of the heat capacity; this behavior is interpreted as the existence of N_L^* with a local TGB_C structure in the low-temperature N^* range.

It appears necessary to use high-resolution methods to observe the above phenomena, whereas classical techniques such as DSC calorimetry [13,35,36], optical microscopy [13,51,52], dielectric spectroscopy [43,52,53], or thermobarometry are not able to detect them.

Finally, with the classical techniques, it is practically impossible to distinguish the N_L^* mesophase, respectively, from the TGB_A one for the $n=10$ compound and from the usual N^* one for the $n=12$ compound.

In the $n=10$, the N_L^* domain shows a strong TGB_A character recently confirmed by x-ray studies [54]. Perhaps, for $n=12$, the N_L^* domain also exhibits a very weak TGB_C character.

V. CONCLUSION

High-pressure measurements have been performed by thermobarometric analysis on six homologous, 9 to 12, 14 and 16, $nF_2BTFO_1M_7$ chiral chemical series. The pressure-temperature phase diagrams have been determined for all compounds. They show that the appearance and/or disappearance of some phases lead to the observation of several singular points. Thus, singular points $Cr-S_C^*-S_A$, $Cr-S_C^*-TGB_C$, and $Cr-TGB_C-TGB_A$ have been shown in these diagrams. Our investigations also show that the pressure can have the same effects on intermolecular interactions as shortening the molecular length. Concerning the multicritical points predicted by Renn and Lubensky, we have again obtained $S_A-TGB_A-N^*$ (B_1), $S_C^*-S_A-TGB_A$ (B_2) and in single component systems we have established the existence of multicritical points $S_C^*-TGB_C-N^*$, $TGB_C-TGB_A-N^*$, and $S_C^*-TGB_C-TGB_A$, denoted, respectively, CEP, L , and B_3 . These results are appreciably in good agreement with Renn and Lubensky's theory.

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