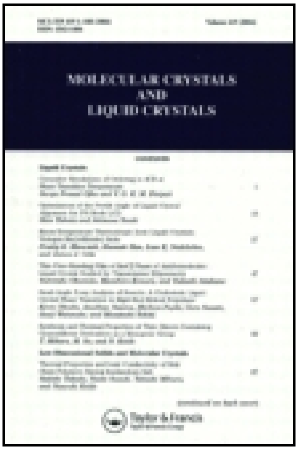

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Thermodynamics of Two Compounds of Chiral Non-Symmetric Dimesogens Under Pressure

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Thermodynamics of Two Compounds of Chiral Non-Symmetric Dimesogens Under Pressure

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High pressure experiments have been performed by thermobarometric analysis on two compounds of chiral non-symmetric dimesogens, which both exhibit the S_C^* and S_A mesophases. The pressure-temperature phase diagrams were determined. Molar volume changes for all phase transitions, and the pressure coefficients at constant volume- of the phases were also deduced from the recorded thermobarograms. The thermobarometric analysis allows us to easily separate the entropy of the phase transition into a configurational part and a part dependent on volume.

1 – 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. Thus recently, a new architecture has been introduced, consisting of two different mesogenic units linked via a flexible spacer [1]. These three-block molecules give rise to very interesting smectic mesophases [2–5]. Also the spacer length plays an important role in both symmetric [6] and non-symmetric systems [2].

In this paper, we report on thermobarometric studies of two chiral non-symmetric dimesogens for which numerous thermodynamic data were still unknown. This work is part of a more general study of the effect of pressure on phase sequences, on thermal stability of phases and on order of transition for new liquid crystal compounds [7–11].

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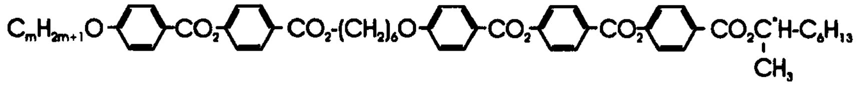
2 - COMPOUNDS

Our choice fell on the homologous series with chiral non-symmetric dimesogens which chemical formula (abbreviated to mBB6BBB8*) is:



Phase identifications and transition temperatures were determined by both thermal microscopy and differential scanning calorimetry under atmospheric pressure [12]. According to both methods, the phase sequences versus the number of carbon atoms (m) in the terminal alkoxy chain are as follows:

$$\mathrm{Cr} - \mathrm{S}_\mathrm{C}^* - \mathrm{I} \quad \text{for } m \leq 13$$

$$\mathrm{Cr} - \mathrm{S}_\mathrm{C}^* - \mathrm{S}_\mathrm{A} - \mathrm{I} \quad \text{for } m \geq 14$$

Cr and I are, respectively, crystalline and isotropic phases. The S_C^* mesophase exists for all compounds over a wide temperature range (between 19 and 48 K). From m = 14, an S_A mesophase is present at high temperatures but on a very narrow domain of temperature (from 1.1 K for m = 14 to 5 K for m = 16) in comparison with the one of S_C^* mesophase. We report here the results of high pressure studies for m =15 and 16 compounds, obtained by the thermobarometric method.

3 - METHOD

Studies of phase transitions were performed under pressure by thermobarometric analysis (TBA) using an automatized metabolemeter (SCERES, MAB 02 A 20). Measurements consisted in recording, versus temperature, the pressure (thermobarogram) of a small sample (about 10 mg) enclosed in a metallic cell. The sample is introduced in the cell in crystalline powder, then melted in liquid phase and finally recrystallized. All the phenomena that appear for liquid crystals are reversible and the treatment has no influence in the following thermodynamic behaviour.

First order phase transitions are accompanied by a sudden increase in pressure as a function of the temperature; the slope of the equilibrium curve (biphasic portion of the thermobarograms) is given by the Clapeyron relation [13]:

$$\left(\frac{dP}{dT}\right)_{tr} = \frac{1}{T}\frac{\Delta H_{tr}}{\Delta V_{tr}} \qquad (1)$$

This relation permits calculations of the change in molar volume ΔV_{tr} when the enthalpy change ΔH_{tr} and transition temperature T are well established.

Outside of the transition domain, the slope of thermobarogram $\left(\frac{dP}{dT}\right)_V$ is

$$\left(\frac{dP}{dT}\right)_V = \frac{\alpha}{\chi} \tag{2}$$

where α and χ characteristic of the single phase are respectively the isobaric expansibility $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and the isothermal compressibility $\chi = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. The details of this technique and interpretations of thermobarograms have been sufficiently described elsewhere [10, 15–17] especially for first order transitions, and more recently for weakly first order or second order transitions in Refs. [7, 8].

The metabolemeter used covers the temperature range between 300 and 500 K and pressures up to about 160 MPa. The scan rates of heating are inferior to 4 $\mathrm{K.min^{-1}}$.

4 - RESULTS

Examples of thermobarograms obtained for m = 15 and m = 16 are reported on Figures 1 and 2 respectively. The different thermobarograms have been recorded by changing the initial experimental conditions of pressure, temperature and scan rates of heating. The heating rate is taken equal to 1 $\mathrm{K.min^{-1}}$. For all thermobarograms, at low temperature, the recorded basic line, corresponds to the expansion (in crystalline phase for Fig. 1b-c and Fig. 2c or in S_C^* mesophase for other cases) of the compound when filling up the free volume comprised between the sample and the cover.

For m = 15, all thermobarograms (Fig. 1) exhibit $S_C^* - S_A$ and S_A-I transitions. The existence of a pressure increment associated to these transitions allows to qualify them as first order ones. The slopes of their equilibrium curves (biphasic portions of thermobarograms corresponding to Clapeyron curve) are about 1.58 MPa $\mathrm{K^{-1}}$ for $S_C^* - S_A$ transition and 1.82 MPa $\mathrm{K^{-1}}$ for S_A-I one. Each thermobarogram of Fig. 1b-c shows at low temperature an abrupt change on slope, which occurs at 357 K, followed by a strong increase on pressure (about 6.5 and 31.8 MPa) associated to the melting $(Cr - S_C^*$ transition); the slope of

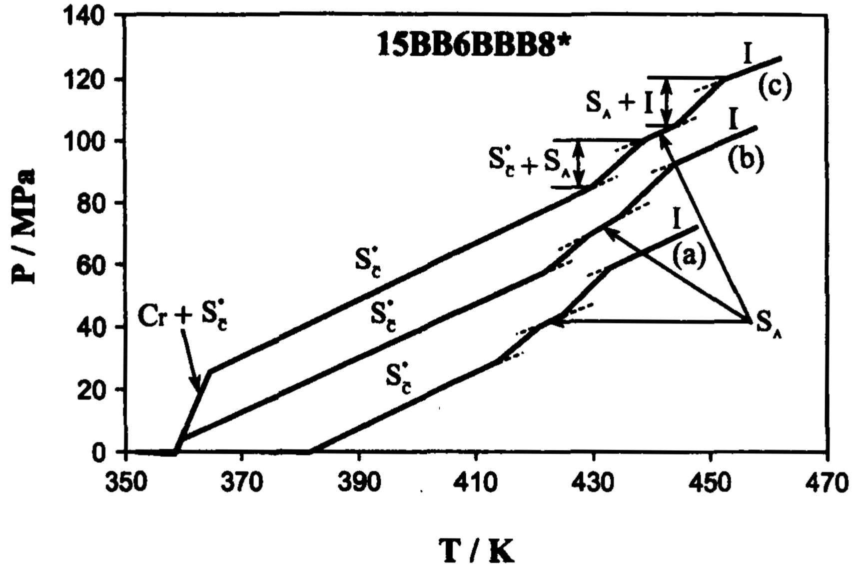


FIGURE 1 Examples of thermobarograms obtained for 15BB6BBB8* showing the mesomorphic polymorphism

the equilibrium curve at $Cr - S_{\tilde{C}}^*$ transition is 2.70 MPa K^{-1}. The average values of slopes $\left(\frac{dP}{dT}\right)_V$ of thermobarograms for $S_{\tilde{C}}^*$, S_A and I phases, far from transitions, are 0.88, 0.96 and 0.67 MPa.K^{-1} respectively.

For m = 16, thermobarograms 2-a and 2-b exhibit two transitions $S_{\tilde{C}}^* - S_A$ and S_A-I which are also first order since they are characterized by increments of the pressure. The slopes of equilibrium curves for $S_{\tilde{C}}^* - S_A$ and S_A-I transitions are about 1.56 and 1.76 MPa K^{-1} respectively. Inside phases and far from transitions, the successive slopes associated to expansion of $S_{\tilde{C}}^*$, S_A and I phases are 0.90, 0.91 and 0.61 MPa.K^{-1}. The last thermobarogram shows a strong increment of pressure at 360 K which corresponds to the melting transition. The pressure decrease observed at the end of the thermobarogram is induced by the escape of a product because the cell sealing was not perfect.

5 – DISCUSSION

The interpretation of thermobarogram networks including several heating runs plotted for different initial conditions led to the pressure-temperature (P-T) phase diagrams. These diagrams presented in figures 3 and 4, are plotted by using mean

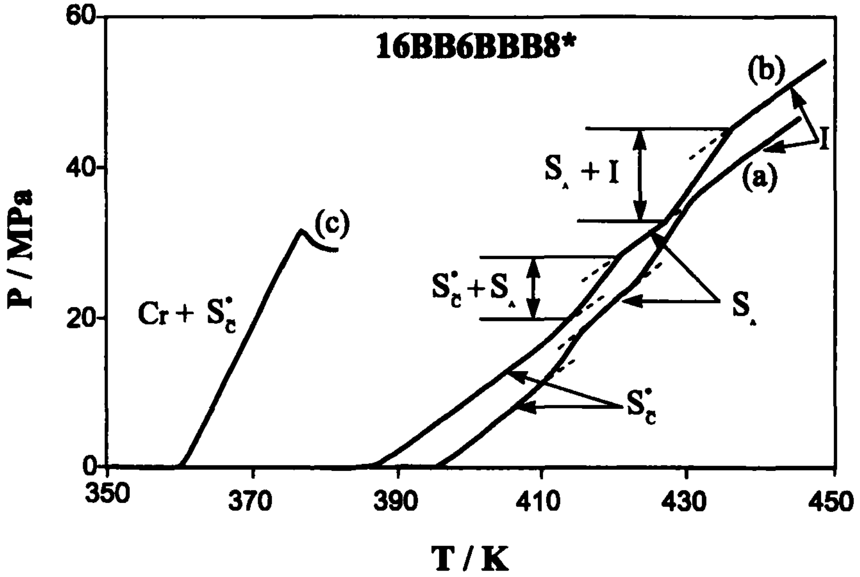


FIGURE 2 Examples of thermobarograms obtained for 16BB6BBB8* showing the mesomorphic polymorphism

values from several thermobarograms for the Clapeyron slopes and for the transition temperature at atmospheric pressure.

The mesomorphic properties and thermodynamic data for each phase and phase transition of both compounds are gathered in Tables I and II. These values are in good agreement with literature data for first order phase transitions.

According to the values of slopes which correspond to $S_C^* - S_A$ and S_A-I transitions, the stability range of S_A mesophase may decrease when pressure increases. Thus, the extrapolation of the $S_C^* - S_A$ and S_A-I line transitions may lead to the prediction of a triple point $S_C^* - S_A - I$. Above this singular point, at constant pressure, upon heating in the S_C^* mesophase, it undergoes a direct transition into the isotropic phase. In a first approximation, if the $S_C^* - S_A$ and S_A-I line transitions were straight lines, the pressure value of triple point would be between 90 and 100 MPa. However, thermobarograms recorded near the limited pressure of our equipment show that the S_A mesophase is always present.

Then, the stability range of S_A mesophase will remain constant or increase more slowly when pressure increases, as it is shown in the P-T phase diagrams.

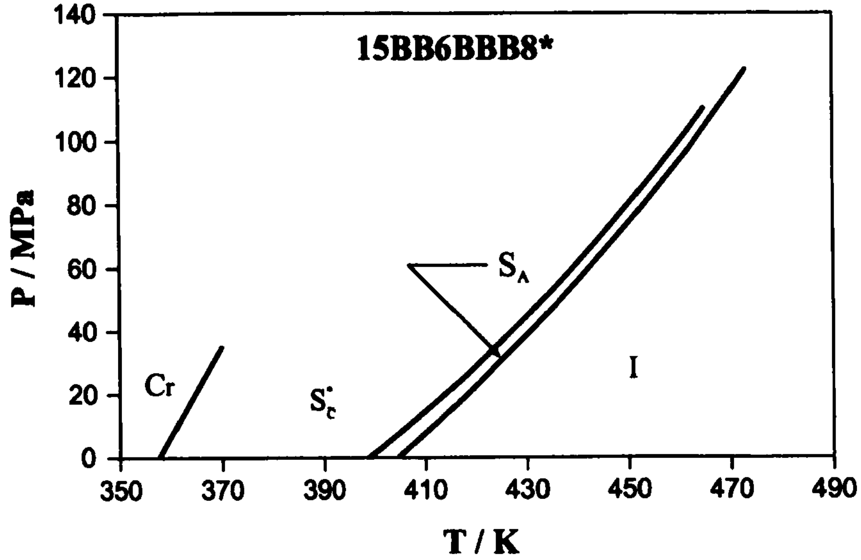


FIGURE 3 Pressure-temperature phase diagram for 15BB6BBB8*

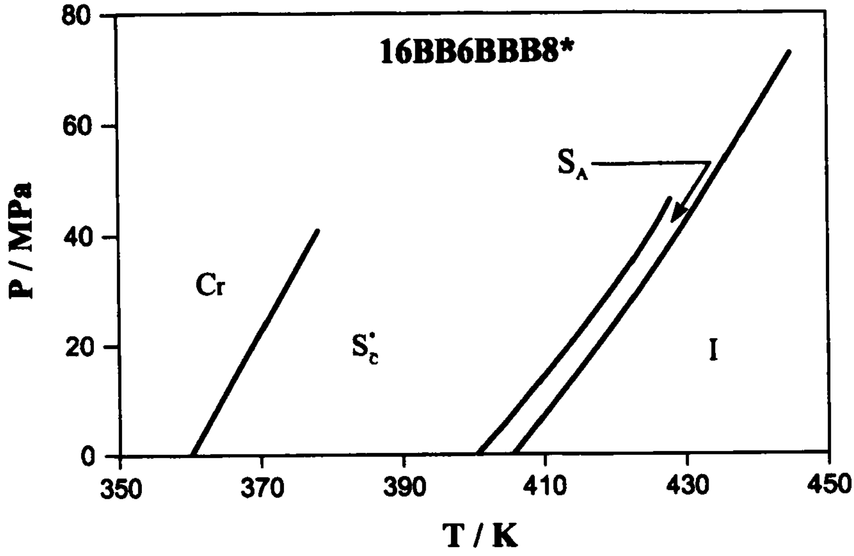


FIGURE 4 Pressure-temperature phase diagram for 16BB6BBB8*

Indeed, on the one hand the values in the tables are average values of several thermobarograms, and on the other hand some thermobarograms also show that the slope of $S_C^* - S_A$ line transition increases very slightly with pressure.

TABLE I Experimental data measured and reported for the phases and transitions of 15BB6BBB8*

Phases	*Cr*		$S^*_{\bar{C}}$		S_A		*I*
15BB6BBB8*	•		•		•		•
T[12]		357		399.6		403	
ΔH_{tr}[12]		44		2.74		7.93	
$\left(\frac{dP}{dT}\right)_V$	–		0.88		0.96		0.67
$\left(\frac{dP}{dT}\right)_{tr}$		2.70		1.58		1.82	
ΔV_{tr}		46		4.2		10.5	

T	Transition temperature (K) under atmospheric pressure;
ΔH_{tr}	Transition enthalpy (kJ.mol^{-1}) under atmospheric pressure
$\left(\frac{dP}{dT}\right)_{tr}$	Slope of boundary lines (MPa K^{-1}) of the P-T phase diagram;
$\left(\frac{dP}{dT}\right)_V$	Slope of thermobarograms out of the transitions (MPa K^{-1});
ΔV_{tr}	Volume change (10^6 m^3 mol^{-1}) for transitions calculated by the Clapeyron equation.

TABLE II Experimental data measured and reported for the phases and transitions of 16BB6BBB8*

Phases	*Cr*		$S^*_{\bar{C}}$		S_A		*I*
16BB6BBB8*	•		•		•		•
T[12]		360		400.7		405.7	
ΔH_{tr}[12]		42		2.99		8.98	
$\left(\frac{dP}{dT}\right)_V$	–		0.90		0.91		0.61
$\left(\frac{dP}{dT}\right)_{tr}$		2.57		1.56		1.76	
ΔV_{tr}		45		4.8		12.7	

It is possible to separate the entropy ΔS_{tr} of the phase transition into configurational entropy $\Delta_{conf}S$ when the volume does not change, and the entropy $\Delta_V S$ due to the volume change at phase transition [18, 19]. The relationships between these three quantities is

$$\Delta S_{tr} = \Delta_{conf} S + \Delta_V S \qquad (3)$$

where $\Delta_V S$ is given by

$$\Delta_V S = \int_{V_1}^{V_2} \left(\frac{dP}{dT}\right)_V dV \tag{4}$$

If the quantity in parentheses is nearly constant, the result of the integration is

$$\Delta_V S = \left(\frac{dP}{dT}\right)_V \Delta V_{tr} \tag{5}$$

That is the case for recorded thermobarograms (Figs. 1 and 2).

The ratio between $\Delta_{conf} S$ and $\Delta_V S$ can be written

$$\frac{\Delta_{conf} S}{\Delta S_{tr}} = 1 - \frac{\Delta_V S}{\Delta S_{tr}} = 1 - \frac{\left(\frac{dP}{dT}\right)_V}{\left(\frac{dP}{dT}\right)_{tr}} \tag{6}$$

where we have used Equations (1) and (5). The thermobarometric method used here allows us to determine easily this ratio from the recorded thermobarograms. The results are listed in Tables III and IV.

TABLE III Experimental data concerning contributions of the configurational part of entropy and volume-dependent part, at atmospheric pressure, of 15BB6BBB8*

Transitions	$\frac{\Delta_{conf} S}{\Delta S_{tr}}$	$\frac{\Delta S_{tr}}{J.K^{-1}.mol^{-1}}$	$\frac{\Delta_{conf} S}{J.K^{-1}.mol^{-1}}$	$\frac{\Delta_V S}{J.K^{-1}.mol^{-1}}$
15BB6BBB8*				
$S_C^* - S_A$	0.42	7.5	3.2	4.3
S_A-I	0.48	22.4	10.8	11.6

TABLE IV Experimental data concerning contributions of the configurational part of entropy and volume-dependent part, at atmospheric pressure, of 16BB6BBB8*

Transitions	$\frac{\Delta_{conf} S}{\Delta S_{tr}}$	$\frac{\Delta S_{tr}}{J.K^{-1}.mol^{-1}}$	$\frac{\Delta_{conf} S}{J.K^{-1}.mol^{-1}}$	$\frac{\Delta_V S}{J.K^{-1}.mol^{-1}}$
16BB6BBB8*				
$S_C^* - S_A$	0.44	6.6	2.9	3.7
S_A-I	0.53	19.1	10.1	9.0

For both $S_C^* - S_A$ and S_A-I transitions, the $\Delta_{conf} S$ was found to be significant, ranging from 42 to 53 % of the total transition entropy observed under atmospheric pressure. These results suggest that the configurational contribution is an important factor involved in the phase transition of these chiral non-symmetric dimesogens. However, these values are comparable to the values obtained for other types of compounds as alkylcyanobiphenyls (nCB for n=6 and 7) [19]. Since, for the S_A mesophase, the layer spacing is slightly less than the molecular length, indicating a bent shape for molecules [12], and is almost constant versus temperature [12]; then the flexible spacer could not play a role in the configurational distributions in these two compounds.

In order to identify the molecular factors responsible for the configurational distribution, we must discuss how behaviors of mesophases depend on the spacer and alkoxy chain. In a preceding work [12], two separate homologous series of chiral non-symmetric dimesogens were investigated. In these systems, the spacer length and the alkoxy chain length play an important role since a rich variety of smectic phases are displayed with their variations. Indeed, when the spacer is even, i.e. the number of carbon atoms involved in the spacer is even, the molecules are of a rod-like conformation and S_A and various S^*_C mesophases (S^*_{CA}, S^*_{CFI}, S^*_C, $S^*_{C\alpha}$) have been identified, whereas when the spacer is odd (it is the case of this paper) the molecules are bent and S_A and $S^*_{\bar{C}}$ mesophases have been observed and characterized.

The chemical series with the odd spacer show the stabilization of the S_A mesophase above the $S^*_{\bar{C}}$ mesophase when the length of the alkoxy chain increases. This result seems to indicate that the chain is flexible enough to balance the bent shape of the molecule. This flexibility allows describing the configurational distribution.

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