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## Liquid Crystals

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# Pressure effect on the nematic–isotropic transition in dilaterally substituted nematogens

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The effect of pressure on the liquid crystal properties of two new dilaterally substituted nematogens has been studied. The method employed involves measurement of the thermal pressure variation of a sample under isochoric conditions. The pressure–temperature phase diagrams were determined. As for unsubstituted compounds, the nematic phase is stabilized upon application of pressure. The values of the  $(\partial T/\partial P)^{n^1}$  slopes of the clearing lines for these nematogens are, however, significantly higher than those generally characterizing rod-shaped nematics. The entropy separation method was used to estimate the constant volume and the volume-dependent terms of the entropy changes at the nematic–isotropic transition. The values of these contributions were determined on the basis of thermobarometric data showing that the transition entropy is strongly volume-dependent. This suggests that the higher values of the  $(\partial T/\partial P)^{n^1}$  slopes observed for these compounds can be related to the rearrangement of the lateral flexible chains in the nematic phase when the pressure increases, leading to a decrease of the excluded free volume caused by the bulky core of the molecules.

## 1. Introduction

In thermotropic liquid crystals, the nematic order is essentially due to the anisotropic intermolecular potentials, which are strongly density-dependent. The nematic ordering usually takes place when a minimum density, which is pressure- (or temperature-) dependent, is obtained. For common nematic compounds, the molecules present a rod-like shape usually composed of a main aromatic core with terminal flexible chains. However, several studies have shown interest in compounds having larger cores [1] or lateral substituents, which are introduced on the rigid core [2–9] leading to molecules deviating from the classic shape. It has been shown recently that when lateral alkoxy substituents are introduced on a four-ring aromatic core, a wide enantiotropic nematic range is obtained [3–7]. Previous  $^{13}\text{C}$  NMR studies pointed out that in the nematic field these lateral substituents adopt a mean conformation nearly parallel to

the molecular long axis and, therefore, the anisotropic packing required for the nematic stability remains nearly unchanged.

The nematic properties of this kind of compound are a function of the tail and the nature of the lateral substituents [1–4]. This feature has been explained on the basis of the lateral chain conformation in the nematic phase. This conformation makes the molecules bulkier and, because of the steric repulsive forces between the lateral chains, increases the excluded free volume. This suggests that changing the density of these compounds might provide additional information towards understanding their mesomorphic properties. Here we extend the study of the nematic order of laterally substituted nematogens using pressure as a thermodynamic parameter. In this work, we focus on the questions of how the clearing transition depends on pressure, and whether the thermodynamic characteristics of this transformation differ from those of nematics with a classical rod-like shape.

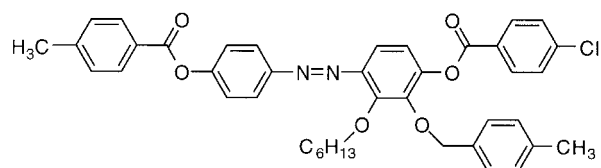
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For this purpose, we use a thermobarometric method [10–12] that involves the measurement of the thermal pressure variations of a sample at different constant volumes. The liquid crystals chosen for this study are two dilaterally substituted nematogens which are presented in the first section.

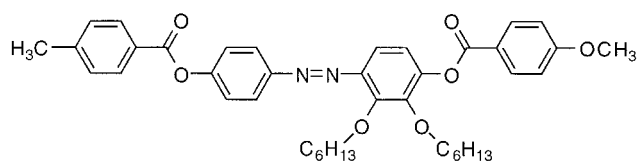
## 2. Experimental

### 2.1. Materials

For our studies, two nematogenic compounds were investigated: 2-(4-methylbenzoyloxy)-3-*n*-hexyloxy-4-(4'-chlorobenzoyloxy)-4'-(4'-methylbenzoyloxy)azobenzene, denoted 4CH3, and 2,3-di-*n*-hexyloxy-4-(methoxybenzoyloxy)-4-(4-methylbenzoyloxy)azobenzene, denoted 0POE. The detailed procedure for the synthesis of these compounds is given in [7, 9]. For 4CH3 and 0POE, the main core of the molecule contains four aromatic rings, with two lateral substituents on the same side of the one of the inner rings. Their molecular structures are given below:



(4CH3)



(0POE)

These compounds were chosen to quantify the effect of the bulkiness of the lateral substituents on the pressure dependent transitions.

### 2.2. Apparatus

At atmospheric pressure, the phase identification and transition temperatures were determined using a Leica DMRXP polarizing optical microscope (POM), equipped with a Chaix-Meca heating-cooling stage, and a differential scanning calorimeter (Seiko Instrument DSC 220C). For both experiments, heating rates of  $1^\circ\text{C min}^{-1}$  were used. To study the effect of pressure on the phase behaviour, thermobarometric analysis (TBA) was used. This method consists in recording the pressure variation versus temperature (thermobarogram) of a

sample (about 10 mg) at constant volume. The measurements were carried out with an automated metabolemeter (Solutronic MAB 02A20) allowing studies up to 2 kbar in a temperature range from  $-40$  to  $+240^\circ\text{C}$ . The complete TBA set-up and interpretation of the thermobarograms have been extensively discussed in previous papers [10–12]. As for the POM and DSC measurements, heating rates of  $1^\circ\text{C min}^{-1}$  were used for the thermobarometric analysis.

## 3. Results and discussion

### 3.1. DSC measurements

A DSC heating scan for 4CH3 is presented in figure 1. Two peaks are observed representing the melting crystal (Cr)–nematic (N) transition at lower temperature, followed at higher temperature by the clearing nematic–isotropic (I) transformation. DSC thermograms of 0POE exhibit a similar shape. The transition temperatures ( $T_0^{\text{Cr-N}}$  and  $T_0^{\text{N-I}}$ ) and related enthalpy changes ( $\Delta H_0^{\text{Cr-N}}$  and  $\Delta H_0^{\text{N-I}}$ ) for 4CH3 and 0POE are given in table 1. It should be noted that on cooling, crystallization usually does not occur for the two compounds and an extensively supercooled nematic phase is then observed at room temperature. In order to get reproducible measurements, isotherms were done so that the crystalline phases were systematically obtained.

### 3.2. Thermobarometric measurements

Thermobarometric measurements were carried out on the two compounds. In figure 2 the thermobarogram of 0POE shows the Cr–N transition, obtained on heating. The strong pressure increase (with rates of about 27 and 36 kbar  $^\circ\text{C}^{-1}$  for 0POE and 4CH3, respectively) represents the pressure changes during the melting process (Cr + N). An abrupt change of the slope occurs characterizing the end of the phase transformation. An example of the thermodynamic paths obtained along separate isochors by heating a sample of 0POE is presented in figure 3. The phase change revealed by a pressure increment ( $\Delta P$ )<sup>N1</sup> corresponds to the clearing transition. Exploitation of several isochors leads to the determination of the pressure dependence of the phase transition temperatures, which are displayed in figures 4(a) and 4(b) for 0POE and 4CH3, respectively.

Table 1. Phase sequences, transition temperatures ( $^\circ\text{C}$ ) and enthalpy changes ( $\text{kJ mol}^{-1}$ ) for 4CH3 and 0POE.

| Compound | Cr | $T_0^{\text{Cr-N}}$ ( $\Delta H_0^{\text{Cr-N}}$ ) | N | $T_0^{\text{N-I}}$ ( $\Delta H_0^{\text{N-I}}$ ) | I |
|----------|----|--|---|--|---|
| 4CH3     | •  | 115<br>(29.2)                                      | • | 159.8<br>(0.45)                                  | • |
| 0POE     | •  | 110.7<br>(26.8)                                    | • | 160.6<br>(0.60)                                  | • |

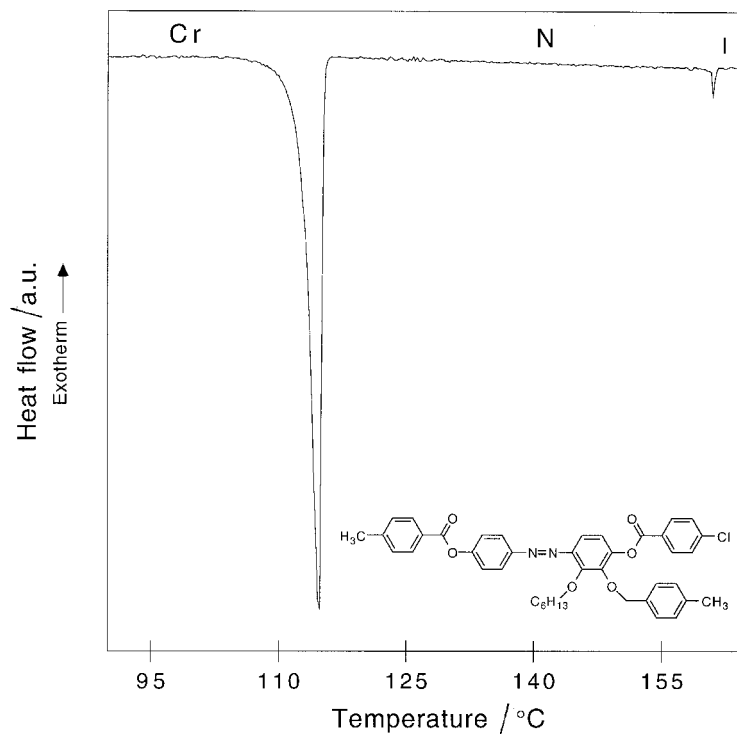


Figure 1. DSC thermogram for 4CH3.

The  $(\partial T/\partial P)^{N1}$  slopes of the measured clearing lines are given in table 2 for the two compounds. Since this is the first study under pressure of these dilaterally substituted liquid crystals, the values of the  $(\partial T/\partial P)^{C+N}$  slopes of the melting curves are also included in table 2. Using the experimental data, the relative volume changes at the clearing transition can be evaluated from the following relation [10]:

$$\frac{\Delta V^{N1}}{V^N} = (\Delta P)^{N1} \alpha^N [(\partial T/\partial P)_V^N - (\partial T/\partial P)^{N1}] \quad (1)$$

where  $\alpha^N$  and  $(\partial T/\partial P)_V^N$  are, respectively, the expansivity and the thermal pressure variation of the nematic phase. We have also evaluated the specific volume change  $\Delta V_0^{N1}$  for the N–I transformation under atmospheric pressure from the Clausius–Clapeyron equation:

$$\Delta V_0^{N1} = \Delta S_0^{N1} (\partial T/\partial P)^{N1} \quad (2)$$

where  $\Delta S_0^{N1} = \Delta H_0^{N1}/T_0^{N1}$  is the entropy change at the clearing transition under atmospheric pressure. Table 2 gives the experimental data and the calculated values for the two compounds.

The entropy change under constant pressure,  $\Delta S_0^{N1}$ , at a nematic–isotropic transition can be expressed as a sum of two contributions [13, 14]:

$$\Delta S_0^{N1} = (\Delta S_0^{N1})_v + (\Delta S_0^{N1})_d \quad (3)$$

where  $(\Delta S_0^{N1})_v$  is the transition entropy at constant volume (configurational contribution) which is related to the variation of the orientational distribution of the molecules, and  $(\Delta S_0^{N1})_d$  is the contribution caused by the volume change (dilatational contribution) at the N–I phase transition. Using the thermodynamic relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (4)$$

Table 2. Selected experimental data for the nematic phase and the nematic–isotropic transition. The expansivity values of 4CH3 and OPOE are unknown; therefore, according to [10], we have used a mean value ( $\alpha^N = 8.3 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ ) for the mesomorphic phases. The  $(\partial T/\partial P)_V^N$  values are deduced from the experimental thermobarograms.

| Compound | $(\partial T/\partial P)^{C+N}$<br>/ $^\circ\text{C kbar}^{-1}$ | $(\partial T/\partial P)_V^N$<br>/ $^\circ\text{C kbar}^{-1}$ | $(\partial T/\partial P)^{N1}$<br>/ $^\circ\text{C kbar}^{-1}$ | $(\Delta P)^{N1}$ /bar | $\Delta V^{N1}/V^N$   | $\Delta S_0^{N1}$<br>/ $\text{J mol}^{-1} \text{ }^\circ\text{C}^{-1}$ | $\Delta V_0^{N1}$<br>/ $\text{cm}^3 \text{ mol}^{-1}$ |
|----------|---|---|--|------------------------|-----------------------|--|---|
| 4CH3     | 27.7  | 143.9   | 90   | 40                     | $1.87 \times 10^{-3}$ | 1.03   | 0.93  |
| OPOE     | 37  | 149.5   | 105  | 62                     | $2.28 \times 10^{-3}$ | 1.38   | 1.45  |

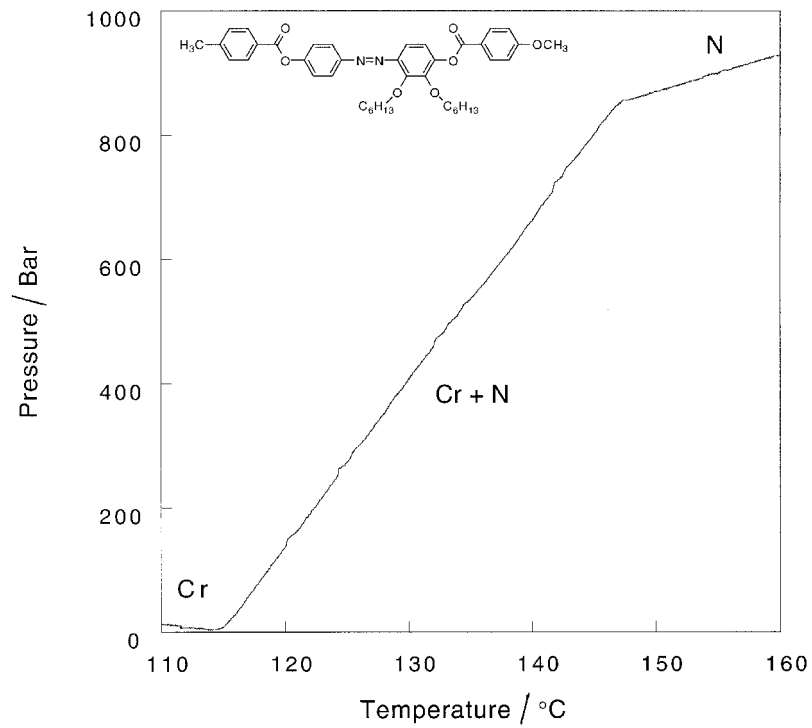


Figure 2. Experimental thermo-barogram showing the melting transition for OPOE.

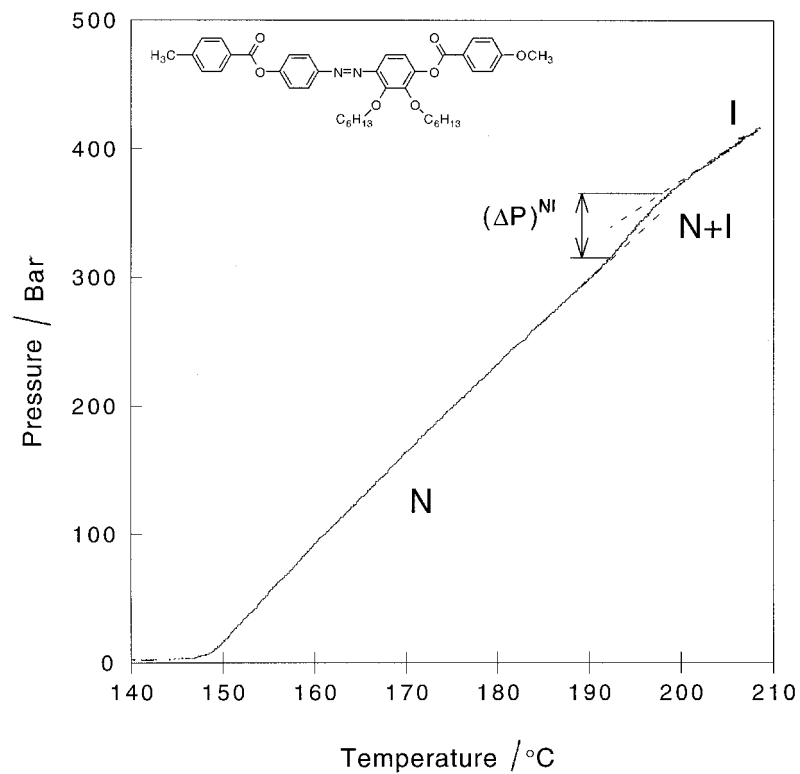


Figure 3. Experimental thermo-barogram showing the clearing transition for OPOE.

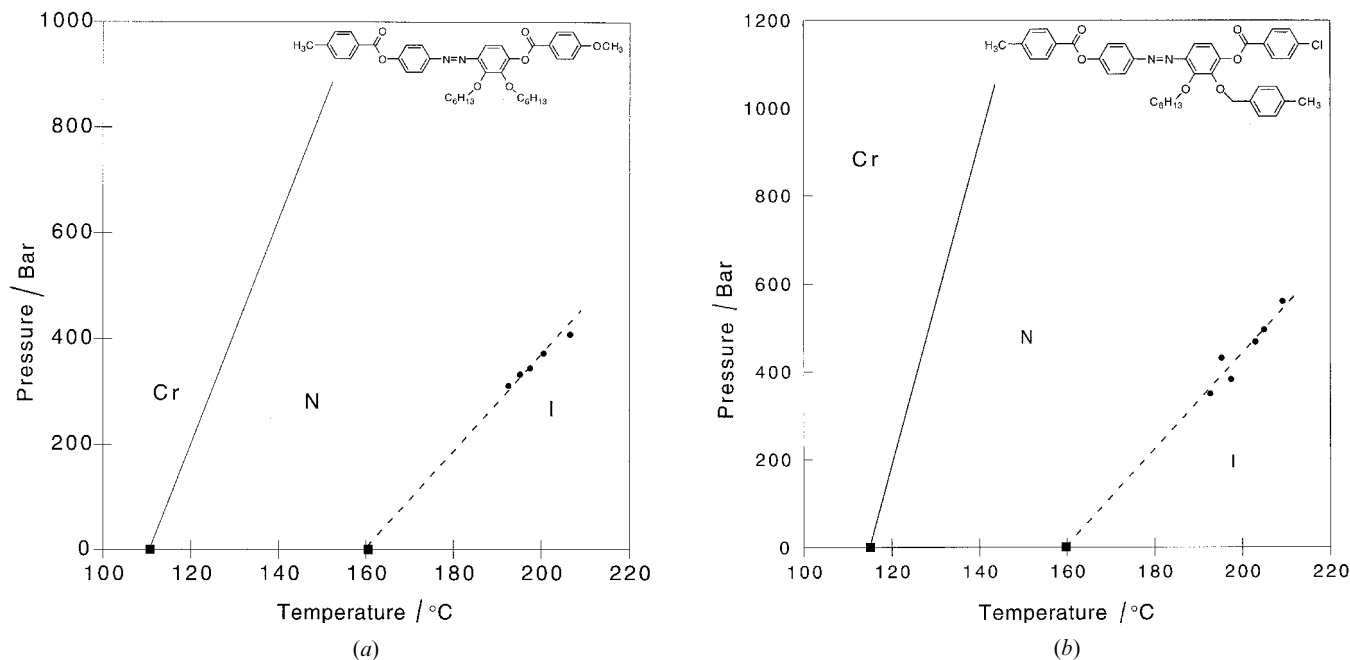


Figure 4. Pressure–temperature phase diagrams for: (a) 0POE, (b) 4CH3. (■) DSC, (—) and (●) TBA.

one can write

$$(\Delta S_0^{N^I})_d = \int_{V_N}^{V_I} (\partial P / \partial T)_v dV. \quad (5)$$

If we assume that  $(\partial P / \partial T)_v$  does not change significantly along an isochoric line, then  $(\Delta S_0^{N^I})_d$  can be expressed as:

$$(\Delta S_0^{N^I})_d = \left( \frac{\partial P}{\partial T} \right)_v^N \Delta V_0^{N^I}. \quad (6)$$

According to the relations (2) and (3), we obtain:

$$\frac{(\Delta S_0^{N^I})_d}{\Delta S_0^{N^I}} = \frac{(\partial T / \partial P)^{N^I}}{(\partial T / \partial P)_v^N} \quad (7)$$

$$\frac{(\Delta S_0^{N^I})_v}{\Delta S_0^{N^I}} = 1 - \frac{(\partial T / \partial P)^{N^I}}{(\partial T / \partial P)_v^N}.$$

Table 3 gives the values of  $(\Delta S_0^{N^I})_v$  and  $(\Delta S_0^{N^I})_d$  for 4CH3 and 0POE, evaluated using our thermobarometric data (table 2).

The  $(\Delta S_0^{N^I})_d$  contribution is found to be significant; it is estimated at 62% and 70% of the total transition entropy observed under constant pressure for 4CH3 and 0POE, respectively. In previous studies [13–16], the same procedure was applied to evaluate the volume-dependent part of the entropy changes at the nematic–isotropic transition for non-substituted nematics. For these systems, the authors reported a value of approximately 50% for the ratio  $(\Delta S_0^{N^I})_d / \Delta S_0^{N^I}$  which is smaller than that we have found for 4CH3 and 0POE.

In figures 4(a) and 4(b), it clearly appears that the domain of thermodynamic stability of the nematic state increases with increasing pressure for the two compounds. This is qualitatively the same behaviour as for rod-shaped nematogens [15–18]. There is, however, a remarkable difference in magnitude for the  $(\partial T / \partial P)^{N^I}$  slopes between 4CH3 and 0POE and those nematogens with classical rod-like shape (typically less than  $50^\circ\text{C kbar}^{-1}$ ). This behaviour can be explained if one considers two aspects: first the bulky shape of the molecules due to the lateral chain conformation in the nematic phase, a property which induces steric repulsions between molecules; secondly, the enhanced density of the nematic phase as a consequence of the pressure increase, which is rather a thermodynamic aspect.

According to Savithramma *et al.* [19] and Singh *et al.* [20], the orientational order in the nematic phase is a result of the superposition of the long range attractive part and the short range repulsive part of the intermolecular potential. The nematic order cannot exist below a critical minimum density of the nematic phase. Increasing the pressure will lead to an increase in the density. This increase in the density will extend the range of the nematic phase. The values of the minimum density favourable to the nematic order essentially affect the pressure dependence of the clearing temperature. Indeed, according to theoretical studies [19, 20], it has been shown for nematogenic compounds that the higher the minimum density, the lower the  $(\partial T / \partial P)^{N^I}$  slopes. This

general behaviour seems to be experimentally confirmed for nematogenic compounds having chemically different molecules with different shapes [1–4].

In this respect, the higher values of the  $(\partial T/\partial P)^{N1}$  slopes found for 4CH3 and OPOE seem to imply that the minimum density required for the nematic order should be lower for these laterally substituted compounds compared with systems with a rod-like shape. This behaviour can be explained in the following manner. As mentioned above, in the nematic phase the lateral substituents are folded back along the mesogenic core; this configuration makes the molecules bulkier. It is, therefore, conceivable that packing an assembly of molecules in the nematic phase will occur with a lower density due to the increase of the excluded free volume caused by steric repulsion between the lateral substituents. Despite the relatively low molecular packing, the mesogenic core is long enough to preserve the nematic order. Enhancing pressure mainly reduces the intermolecular distances; this could constrain the lateral substituents to adopt a more stretched conformation, and the excluded free volume might therefore become smaller. Consequently, the molecules become more closely packed and the nematic structure is stabilized. This analysis is supported by the values of the  $(\Delta S_0^{N1})_d$  contribution reported in table 3 which indicate the strong volume dependence of the entropy of these compounds. So, we believe that the higher values of  $(\partial T/\partial P)^{N1}$  exhibited by these compounds are a consequence of the fact that the enhanced density, as a result of the pressure increase, is mainly ensured by the rearrangement of the lateral substituents of the molecules.

The  $(\partial T/\partial P)^{N1}$  value found for OPOE is higher than that found for 4CH3; this may be partly due to the aromatic nature (more attractive forces) of one of the lateral substituents of 4CH3, which enhances the molecular packing. This explanation is supported by the results for the relative volume changes (table 2) at the N–I transitions for the two compounds, according to theoretical studies [19, 20] which predict the decrease of  $\Delta V^{N1}/V^N$  with increasing molecular packing in the nematic phase. The more pronounced effect of pressure on  $T^{N1}$  for OPOE can also be explained by the higher flexibility of the lateral hexyloxy chain compared with the lateral aromatic branch. It is worth noting that the opposite behaviour has

been observed for non-laterally substituted nematogens [17, 18]. In fact, for homologous series the pressure effect on the nematic order is found to be less pronounced for homologues with longer terminal flexible chains. To explain that, the authors have suggested that, because of the smaller ratio of the rigid core to the flexible chain, the decrease with increasing pressure of the molar volume can also be brought about by a closer packing or coiling up of the terminal chains.

#### 4. Conclusion

To summarize, we have performed pressure experiments using the thermobarometric method on two dilaterally substituted nematogens. The pressure–temperature phase diagrams and the thermodynamic properties of the N–I transition were determined. As for laterally non-substituted nematogens, the stability domain of the nematic phase is enhanced by application of pressure. There are, however, remarkable differences in the magnitude of the  $(\partial T/\partial P)^{N1}$  slopes of the clearing lines, which are higher for the compounds we have studied than for rod-shaped nematogens. The entropy changes at the N–I transition were separated into configurational and volume-dependent contributions. The values of these contributions were determined on the basis of the thermobarometric data, and show a strong volume dependence of the entropy changes at the clearing transitions. We suggest as an explanation of this behaviour that the increase of the density with increasing pressure could be partly explained by the conformational changes of the lateral flexible chains. Thus, the excluded free volume caused by the lateral substituents becomes smaller and the molecules become more closely packed. Consequently, the orientational order in the nematic phase is favoured in comparison with that in the isotropic liquid phase. This is merely reflected, from a macroscopic point of view, by the higher values of the  $(\partial T/\partial P)^{N1}$  slopes.

In order to get more experimental information, further investigations on other systems with two lateral alkoxy chains are in progress.

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Table 3. Entropy changes  $(\Delta S_0^{N1})_v$  and  $(\Delta S_0^{N1})_d$  for the nematic–isotropic transition for 4CH3 and OPOE.

| Compound | $(\Delta S_0^{N1})_v$<br>/J mol <sup>-1</sup> °C <sup>-1</sup> | $(\Delta S_0^{N1})_d$<br>/J mol <sup>-1</sup> °C <sup>-1</sup> |
|----------|--|--|
| 4CH3     | 0.39   | 0.63   |
| OPOE     | 0.41   | 0.96   |

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