

PVT Measurements on 3-Cyanobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate up to 250 MPa and 423 K

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P, *V_m*, *T* data have been measured for the nematic and isotropic phases of 3-cyanobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate between 273 and 423 K and up to 250 MPa. The volume changes accompanying the crystal – nematic and nematic – isotropic transitions have been determined. The corresponding enthalpy changes have been calculated using the Clausius-Clapeyron equation. The *p*, *V_m*, *T* data enable also to estimate the volume entropy for the nematic-isotropic transition. It is found that the configurational part of the transition entropy amounts to 80%, this portion being distinctly larger than found in previous studies for conventional rod-like liquid crystals.

Key words: Aryl-branched Liquid Crystals; High Pressure; *pVT*; Phase Transitions; Thermodynamics.

1. Introduction

In recent papers we reported *p*, *V_m*, *T* data for *n*CBs and *n*PCHs [1–4], which are conventional representatives of rod-like liquid crystals. The substances were chosen because of their stability and polymorphism at moderate temperatures. In this paper we extend the study to a laterally aryl-branched liquid crystal, which displays a nematic phase at about 100 °C. It is 3-cyanobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate (3CNBOB), the phase diagram of which was recently studied by DTA [5] and DSC [6]. Figure 1 shows the structure of this wedge-shape molecule which differs significantly from the rod-like liquid crystals. The mesophase stability despite its unconventional length-to-breadth ratio and the unusual mixing behaviour [7] suggests a sensitive density dependence of the phase behaviour. Therefore we performed volume measurements in the nematic and isotropic phases of 3CNBOB, in order to get more insight in the steric conditions of the mesogenic properties.

2. Experimental

A new high-pressure dilatometer was constructed [8], similar to a previously used apparatus [9], but the pressure transmitting compressed argon is replaced by compressed oil. Furthermore the new design enables us to achieve higher temperatures up to 200 °C. In the present

study the measurements are restricted to 150 °C because a sealing made of indium is used for the dilatometric cell (see Fig. 1 in [1]). Any volume change causes a displacement of a piston that is measured inductively with a Hottinger amplifier alpha spider 8 connected to a personal computer. For details of the data recording, corrections and calibrations see [8].

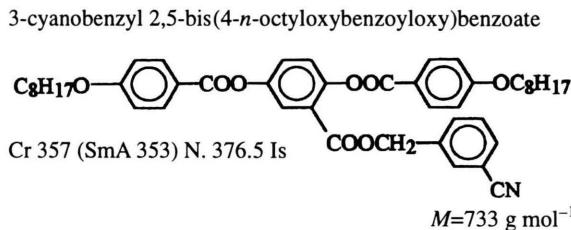


Fig. 1. Structure of 3CNBOB.

In general a measurement is performed after pressurizing to the highest pressure and then recording the volume changes with decreasing pressure at constant temperature. Each pressurizing for a new isotherm starts from ~ 5 MPa. Using the gas-compressed autoclave there is always a risk that the compressed gas might penetrate through the O-rings and indium sealing, even though to a very small extent. Thus only 1 or 2 isotherms with one filling could be measured. The new device allows to measure several isotherms with the same filling of the dilatometric cell. However it was found that the hysteresis

esis pressure is considerably larger when the pressure is transmitted by compressed oil.

The recorded volume changes are combined with atmospheric pressure densities in order to establish p, V_m, T data in the whole p, T range. The densities at 1 atm were determined with a vibrating tube densimeter Anton Paar DMA 60 by Schmalfuß [10]. The synthesis of 3-cyanobenzyl 2,5-bis(4-*n* octyloxybenzoyloxy)-benzoate has been described in [5, 11].

3. Results

3.1 Measurements at Atmospheric Pressure

Figure 2 shows a DSC measurement (carried out in Halle) when the sample was heated from room temper-

ature. After the melting at ~ 357 K a smaller second peak at ~ 366 K appeared and finally the clearing point at 377 K. Furthermore a metastable smectic A phase was observed on cooling. When the sample is annealed at lower temperatures the melting point is shifted to 364 K [5, 6]. Obviously the polymorphism is complicated by the presence of metastable phases that was avoided in the high-pressure studies (in Bochum). The heat effect of the metastable nematic-smectic A transition was too small to be observed at higher pressures [5].

Figure 3 shows the specific volumes at 1 atm measured with the vibrating tube densimeter (in Halle). The volume step at the clearing temperature, $\Delta V_{NI} = 0.0015 \text{ cm}^3 \text{ g}^{-1}$, has been obtained in fitting the $v(T)$ data to a polynomial of second order for the isotropic phase and first order for the nematic phase. This volume change is

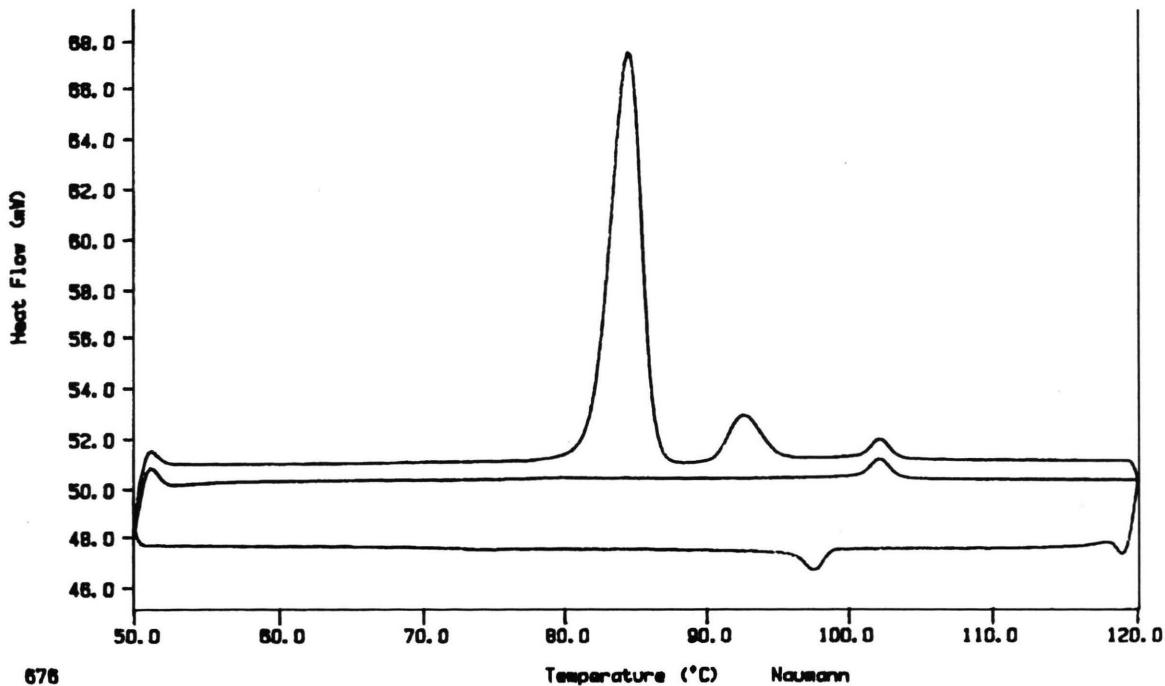


Fig. 2. DSC traces at atmospheric pressure for a not annealed sample of 3CNBOB.

Table 1. Thermodynamic data for the melting of 3CNBOB.

T/K	p/MPa	$\Delta V/\text{cm}^3 \text{ g}^{-1}$	$\frac{(\partial T/\partial p)_{\text{Cr-N}}}{K/\text{MPa}}$	$\Delta H/\text{J g}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$
364.50	0.1	0.0519	0.2958	64.0	46.9
373.15	34	0.0502	0.2845	65.9	48.3
383.15	76	0.0464	0.2704	65.7	48.1
393.15	113	0.0403	0.2581	61.4	45.0
403.15	150	0.0388	0.2457	63.7	46.7
413.15	187	0.0368	0.2334	65.2	47.8
423.15	234	0.0337	0.2177	65.5	48.0

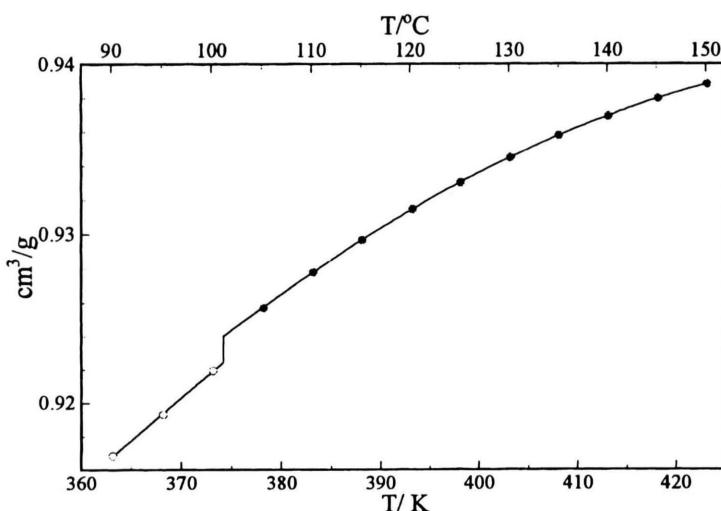


Fig. 3. Specific volume of 3CNBOB at atmospheric pressure after [10].

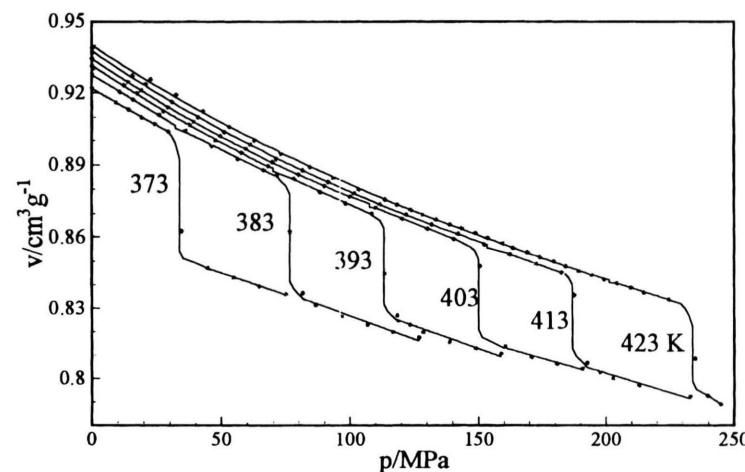


Fig. 4. Specific volume of 3CNBOB as a function of pressure; the steps in the isotherms refer to the transitions Cr \rightarrow N and N \rightarrow Is.

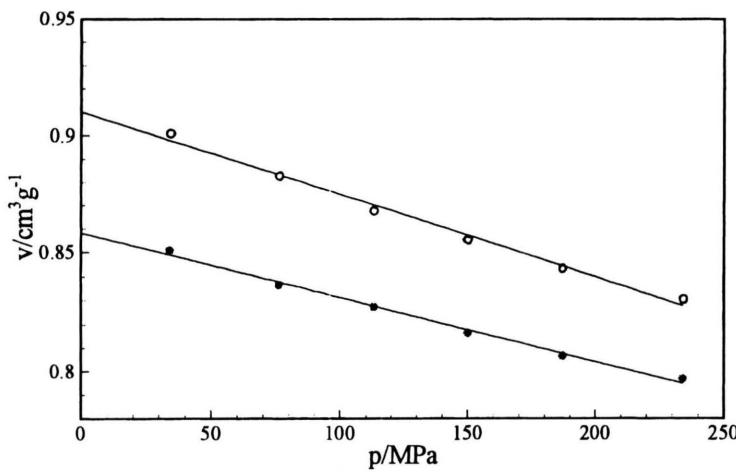


Fig. 5. Specific volume of 3CNBOB along the melting curve for the crystal (●) and nematic (○) phases.

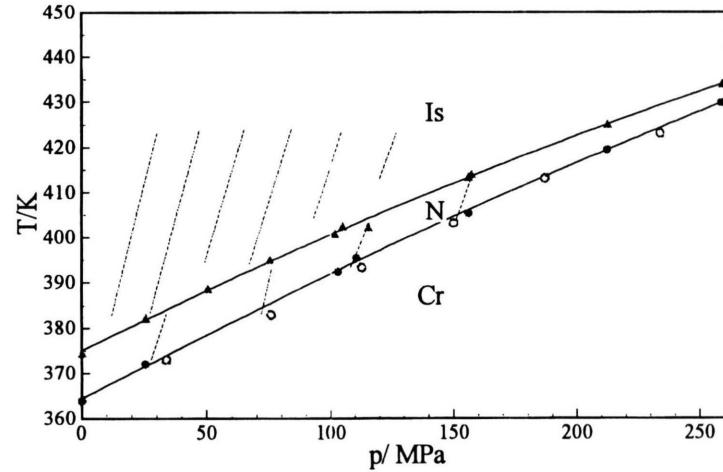


Fig. 6. Phase diagram of 3CNBOB, closed symbols: DTA [5], open symbols: pVT , isochores in the isotropic phase vary from 0.920 to 0.870 in steps of 0.01 cm^3/g , in the nematic phase; 0.905, 0.885, 0.870, 0.855 cm^3/g .

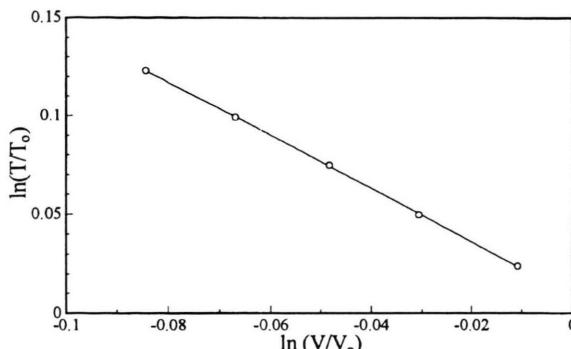


Fig. 7. Logarithm of the clearing temperature against the logarithm of the specific volume along the clearing line; T_0 and v_0 refer to 1 atm.

somewhat smaller than 0.2% reported for rod-like nematogens [1–4].

3.2 Measurements at Higher Pressures

In Fig. 4 the specific volume is plotted as a function of pressure for temperatures between 373.15 and 423.15 K. For these measurements the occurrence of the metastable phase Cr' [5] was avoided by appropriate thermal treatment. The volume step of the nematic-isotropic transition is of the order of the detection limit. It was determined in fitting the isotherms above and below the clearing pressure to polynomials of second order. Thus volume changes of $\Delta V_{NI} \sim 0.001 \text{ cm}^3 \text{ g}^{-1}$ were obtained without a significant pressure dependence. That is, ΔV_{NI} does not seem to die away with increasing pressure, despite its limited resolution.

The volume change of melting was evaluated in a similar manner. The specific volumes at the melting point were obtained by an extrapolation of the isotherms for the nematic and crystal phases, respectively. The corresponding plot in Fig. 5 shows ΔV_{Cr-N} as the distance between the smoothed lines, decreasing from 0.0519 at 1 atm to $0.0355 \text{ cm}^3 \text{ g}^{-1}$ at 200 MPa. Extrapolation of the smoothed curves to atmospheric pressure yields $0.910 \text{ cm}^3 \text{ g}^{-1}$ for the nematic phase and $0.858 \text{ cm}^3 \text{ g}^{-1}$ for the crystal phase. On the other hand, the directly measured value of v_N by Schmalfuß is $0.917 \text{ cm}^3 \text{ g}^{-1}$ at the melting point. Bearing in mind the many fittings and extrapolations of the high pressure measurements the agreement is not too bad.

Some thermodynamic data for 3CNBOB are presented in Table 1, where the enthalpy changes, ΔH_{Cr-N} , have been calculated by use of the Clausius-Clapeyron equation. The slope of the melting curve was taken from Ernst

et al. [5]. ΔH_{Cr-N} decreases somewhat with increasing pressure, although to a less extent than ΔV_{Cr-N} . The enthalpy change at atmospheric pressure can be compared with a DSC study by Masberg [6], who reports 42.2 and 46.1 kJ mol^{-1} for the Cr-N and Cr'-N transitions, respectively.

The melting and clearing temperatures established by Ernst [5], together with those of Table 1 are presented in Figure 6. The pVT melting pressures at a given temperature are somewhat higher than those determined by DTA [5]. This behaviour is also observed in pVT measurements of other compounds [12]. The phase diagram shows also some isochores for the nematic and isotropic phase.

4. Discussion

As in previous papers we compared the slope of isochoric lines, $(\partial p / \partial T)_V$, with the slope of the clearing line, $(\partial p / \partial T)_{NI}$, that enabled us to estimate the configurational part of the transition entropy [13]. In the present work we find $(\partial p / \partial T)_V \approx 0.65 \text{ MPa/K}$ for the nematic phase and $\approx 0.53 \text{ MPa/K}$ for the isotropic phase. The pressure dependence of the clearing temperature, $(\partial T / \partial p)_{NI} \approx (0.25 \div 0.28) \text{ K/MPa}$, is taken from [5]. Thus, $\Delta S_{conf} / \Delta S_{tr} = [(\partial p / \partial T)_{NI} - (\partial p / \partial T)_V] / (\partial p / \partial T)_{NI} \approx 0.8 \div 0.85$. This result is in contrast to findings of conventional rod-like nematogens, where $\Delta S_{conf} / \Delta S_{tr}$ is about 50% [13]. The unusually large value for the configurational part of the transition entropy means that the nature of the nematic–isotropic transition in 3CNBOB is not much influenced by the density. The large difference $(\partial p / \partial T)_{NI} - (\partial p / \partial T)_V$ shows that the density changes significantly along the clearing line. Correspondingly, small values are found for the molecular parameter $\gamma = -\partial \ln T_{NI} / \partial \ln V_{NI}$, which describes the volume dependence of the interaction coefficient after Maier-Saupe ($v = v_0 V^{-\gamma}$) [14]. For 3CNBOB, $\gamma = 1.35$ was derived from the slope of the graph in Figure 7. Similar small values have been found for 4,4'-di-heptyloxyazoxybenzene by Keyes *et al* [15].

Further studies on laterally aryl-substituted liquid crystals are under way in order to get more insight in the steric conditions of the mesogenic properties.

Acknowledgement

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