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## Liquid Crystals

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## Pressure–temperature phase diagrams of smectogenic 4'-alkyl-4-cyanobiphenyls (9CB, 10CB, 11CB and 12CB)

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The pressure–temperature ( $p$ – $T$ ) phase diagrams for four smectogenic members of the 4'-alkyl-4-cyanobiphenyl homologous series ( $n$ CB,  $n = 9, 10, 11$  and  $12$ ) over the temperature range 320–410 K and pressure range 0.1–300 MPa (3 kbar) were constructed using DTA. At 1 atm 9CB exhibits nematic and smectic  $A_d$  phases, while the other members show only the smectic  $A_d$  phase. However, at elevated pressures the clearing line splits in the case of 10CB and 11CB which indicates the induction of a nematic phase. It was found that the triple point, where the isotropic, nematic and smectic phases coexist, is strongly shifted to higher pressures with increasing chain length. This was interpreted as being caused by a loss of the rod-like shape of the molecules containing longer alkyl tails which explore a range of conformations. The slope of the clearing line,  $dT/dp$ , depends strongly on the length of the alkyl chain for the  $n$ CB series, but does not show a step-wise change between the nematogenic and smectogenic members.

### 1. Introduction

4'-Alkyl-4-cyanobiphenyls ( $n$ CBs) are liquid crystalline (LC) materials discovered in the 1970s [1, 2]. The members with  $n = 5–7$  show a nematic (N) phase, those with  $n = 8$  and  $9$  exhibit N and smectic  $A_d$  ( $SmA_d$ ) polymorphism, while for  $n \geq 10$  the  $SmA$  phase appears exclusively [2]. Low transition temperatures (close to room temperature), good chemical stability, and high dielectric anisotropy caused great interest in the study of these materials using a wealth of experimental methods. These investigations however, concerned mainly the members with  $n = 5–8$ .

The phase behaviour observed at ambient pressure may change considerably at elevated pressures [3–11]. In some substances pressure induces new LC phases [5, 6, 8–10], while in others pressure-limited phases are

observed [3–5, 7, 11]. The present investigation of the influence of pressure on the phase diagrams of the higher members of the  $n$ CB series was stimulated by non-linear dielectric effect (NDE) studies reported by Drozd-Rzoska *et al.* for the  $n$ CB series ( $n = 4–12$ ) [12], and the  $n$ -alkylisothiocyanatobiphenyl ( $n$ BT) series [13]. The authors determined the discontinuities,  $\Delta T = T^* - T_{I-LC}$  and  $\Delta p = p_{I-LC} - p^*$ , of the I–N and I– $SmA$  transitions, where  $T_{I-LC}$  and  $p_{I-LC}$  correspond to the clearing temperature and pressure, respectively, while  $T^*$  and  $p^*$  are the extrapolated temperature and pressure of a hypothetical continuous phase transition. It was found that pressure reduces the discontinuity of the  $SmA \rightarrow I$  transition, in contrast to behaviour of the  $N \rightarrow I$  transition. This observation led the authors to conclude that for smectogens the increase in pressure shifts the rod-like molecules along the preferred orientation axes, so destabilizing the molecular arrangements in the smectic layers, and

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thus a nematic phase may be induced. Recently we have performed DTA studies on a few members of two homologous series: the *n*BTs which exhibit the crystal E phase [8, 14], and the 5-*n*-decyl-2-(4'-isothiocyanatophenyl)-1,3-dioxanes (*n*DBTs) which show exclusively the smectic A<sub>1</sub> phase [10]. For the longer members studied, 8BT [8, 9] and 10DBT [10], the smectic-isotropic line split at elevated pressures and a new phase appeared (probably the N phase). The aim of the present study was to check whether similar behaviour could be observed for the smectogenic members of the *n*CB series.

## 2. Experimental

The high pressure DTA devices used and the experimental procedures applied were the same as those described in previous studies [6–11, 14]. The materials investigated were synthesized in the Institute of Chemistry,

Military University of Technology, Warsaw, Poland. The synthetic route was the same as used in the synthesis of 14CB [15]. The purity of the compounds as studied by gas chromatography was better than 99.3%. The phase transition temperatures and the corresponding enthalpies of transitions obtained by DSC measurements at 1 atm are listed in table 1.

## 3. Results

Figures 1(a–d) show typical DTA traces for particular members of the *n*CB series at different pressures, while in figures 2(a–d) the *p*–*T* phase diagrams constructed using these data are given. In the case of 9CB the SmA → N transition was observed over a limited pressure range only; above *c.* 60 MPa it was practically invisible in the DTA traces. The SmA → N transition is a weak first order transition and dies away at higher pressures

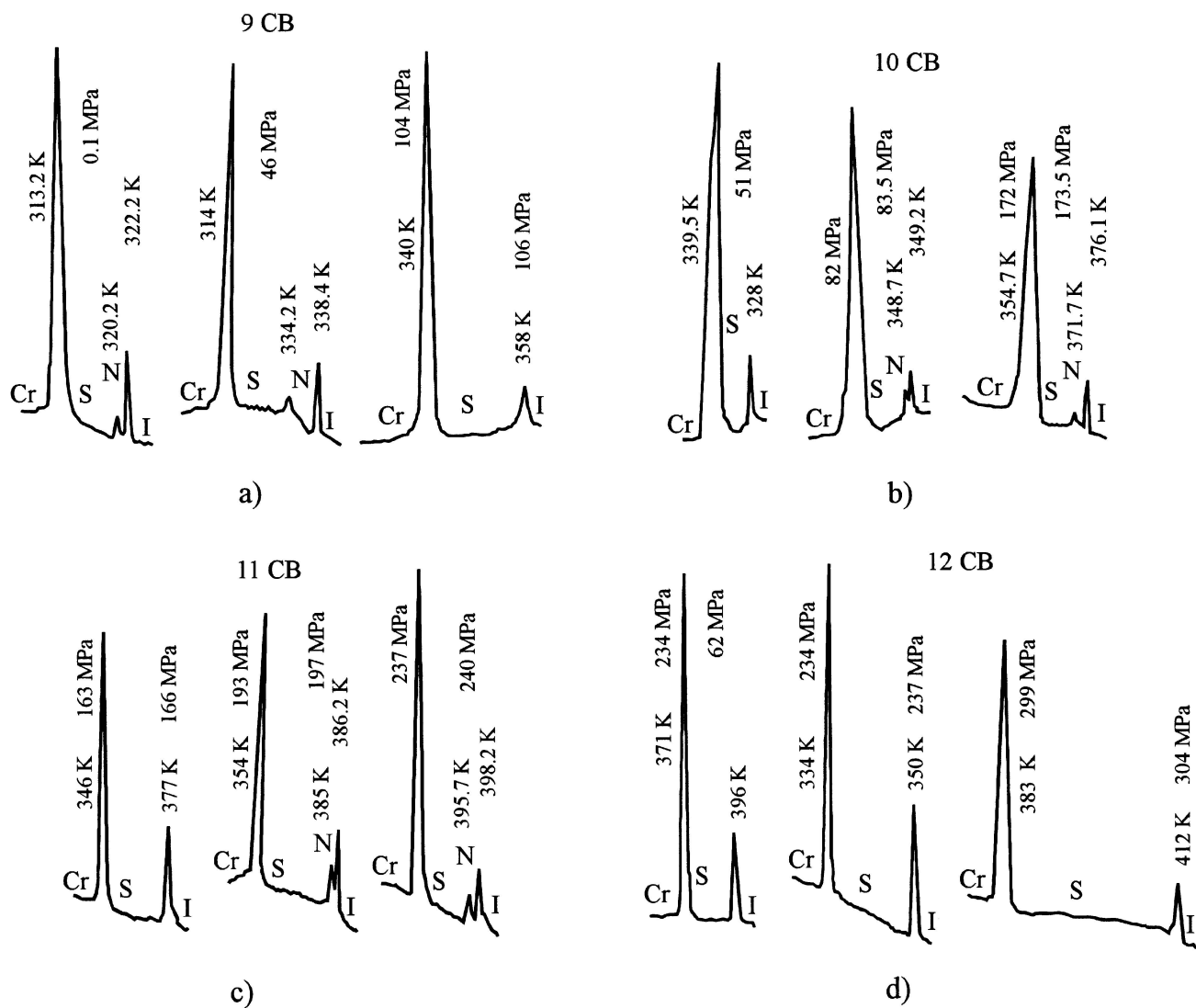


Figure 1. Selected DTA traces for four members of the *n*CB series (S denotes SmA).

Table 1. Phase transition temperatures (K) and the associated enthalpies of the transitions (italics,  $\text{kJ mol}^{-1}$ ) for the *n*CBs measured using DSC at 1 atm (heating rate,  $5 \text{ K min}^{-1}$ ).

Compound	Cr	SmA	N	I
9CB	*	314.9 <i>34.7</i>	* 320.2 <i>0.50</i>	322.2 <i>1.63</i>
10CB	*	316.9 <i>37.2</i>	*	323.6 <i>3.05</i>
11CB	*	325.5 <i>42.7</i>	*	329.5 <i>3.85</i>
12CB	*	318.9 <i>34.9</i>	*	331.0 <i>4.57</i>

(cf. 8CB [16]). For two homologues, 10CB and 11CB, the peaks corresponding to the clearing points are split above 66 and 182 MPa, respectively; see figures 1(b), 2(b) and 1(c), 2(c). Also in these cases the peaks corresponding to the SmA  $\rightarrow$  N transition diminished with pressure. No splitting of the clearing line was observed for 12CB, although the measurements were carried out up to 300 MPa and 420 K.

All the phase transitions were detected also on cooling, although, a linear decrease of the temperature could not be guaranteed in that mode. The transitions between

LC phases were well reproduced on cooling, whereas the freezing point (except for 10CB) showed a marked supercooling; the observed freezing points are displayed by open triangles in figure 2. These vary approximately linearly. It should be mentioned, however, that a systematic study of supercooling effects was not within the scope of this investigation.

The phase transition lines were fitted by polynomials which are shown in table 2. The initial slope of the clearing line,  $b = (dT/dp)_{1\text{atm}}$ , is greatest for the N  $\rightarrow$  I transition (9CB) and smallest for the SmA  $\rightarrow$  I transition (12CB). For 10CB and 11CB the values of the slopes depend upon the range of pressures taken into account in the calculations:  $b$ -values for the pressures up to the triple point ( $p_{\text{tr}}, T_{\text{tr}}$ ), at which the I, N and SmA phases coexist, are larger than in the case when the whole pressure ranges were taken into account (see data for 11CB in table 2). It corroborates the conclusion derived from previous studies [9, 17] that the slopes of the phase transition lines change discontinuously at the triple point. It seems that only in the case of 10CB are the pressure ranges of the SmA  $\rightarrow$  I and N  $\rightarrow$  I lines sufficiently wide to allow for separate calculations of the slopes  $dT/dp$  (table 2). For 10CB and 12CB, the present results can be compared with those determined from the NDE studies [12].

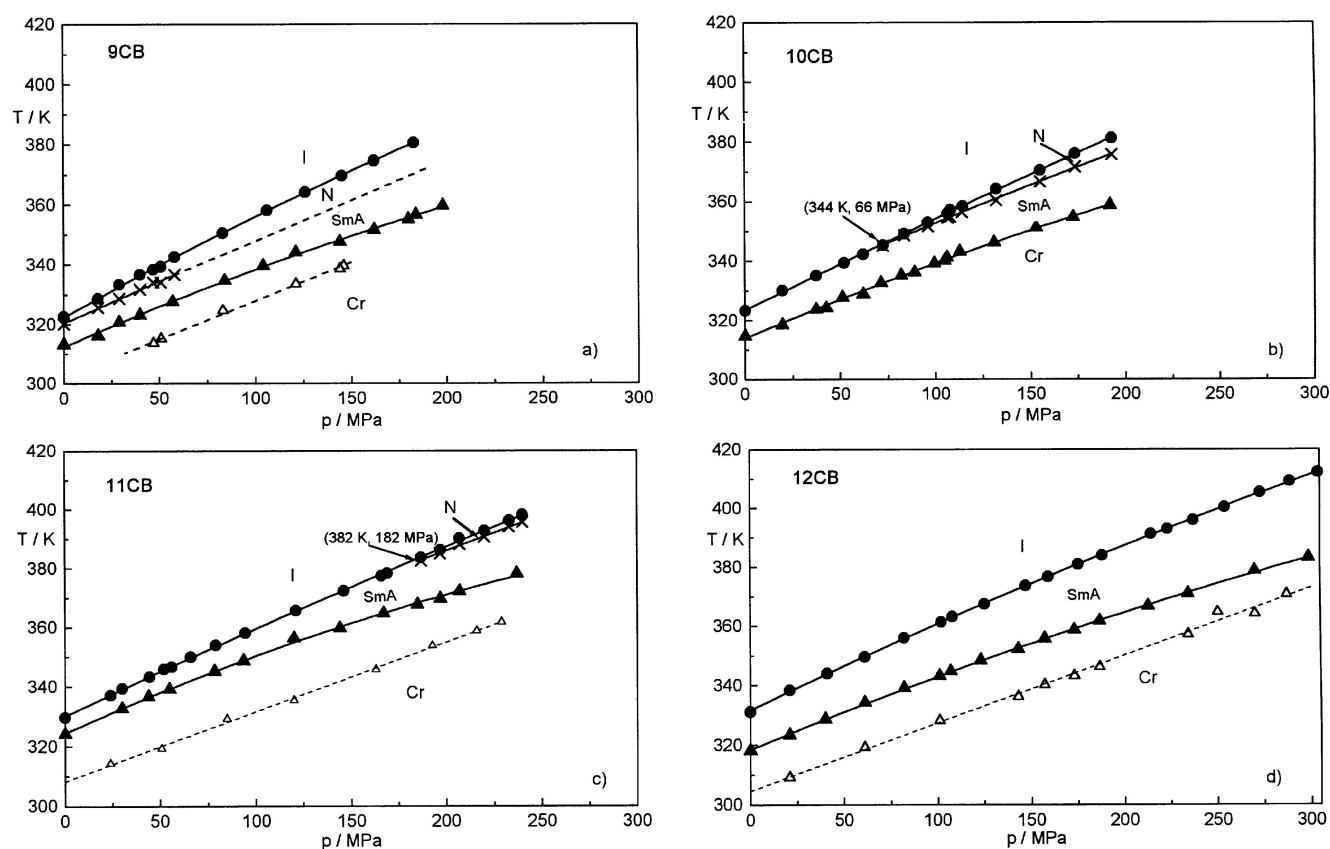


Figure 2. *p-T* phase diagrams of four members of the *n*CB series. Open triangles indicate the freezing points.

Table 2. Transition temperatures,  $T/K = a + b(p/\text{MPa}) + c(p/\text{MPa})^2$ , for the  $n\text{CB}$ s studied with DTA.

Transition	$a$	$b$	$10^4 \times c$	Pressure range/MPa
<b>9CB</b>				
Cr → SmA	312.4	0.284	-2.42	0–198
SmA → N	320.2	0.309	-4.65	0–60
Clearing	322.6	0.354	-2.02	0–183
<b>10CB</b>				
Cr → SmA	313.7	0.277	-2.14	0–192
SmA → N	325.4	0.287	-1.31	71–193
Clearing SmA → I	323.5	0.333	-4.36	0–66
N → I	321.0	0.354	-2.19	66–193
	323.8 <sup>a</sup>	0.315 <sup>a</sup>	0	0–80 <sup>a</sup>
<b>11CB</b>				
Cr → SmA	324.4	0.286	-2.63	0–237
SmA → N	318.2	0.419	-4.02	185–240
Clearing	330.1	0.303	-0.82	0–237
	329.8	0.316	-1.65	0–180
<b>12CB</b>				
Cr → SmA	318.4	0.259	-1.42	0–299
Clearing	331.7	0.304	-1.27	0–304
	330.9 <sup>a</sup>	0.276 <sup>a</sup>	+1.0 <sup>a</sup>	0–245 <sup>a</sup>

<sup>a</sup> From NDE studies [12].

#### 4. Discussion

The most striking result of the present study is the discovery of a pressure-induced nematic phase in smectogenic members of the  $n\text{CB}$  homologous series, as was suggested by Drozd-Rzoska *et al.* [12]. It is a characteristic feature that the pressure corresponding to the triple point depends strongly on the length of the alkyl chain. From figure 2(a) one can suppose that for 9CB the transition lines N → I and SmA → N would intersect at a small negative pressure [18] ( $p_{\text{tr}} \approx -23$  MPa). The same may be said when the phase diagram of 8CB is considered [4, 16], for which a triple point pressure  $p_{\text{tr}} \approx -60$  MPa is obtained by extrapolation of the phase lines. Taking into account the pressures corresponding to the known triple points in the series, one can attempt to predict the triple point for 12CB. Figure 3 (right axis) shows that a quadratic curve can be drawn through the  $p_{\text{tr}}$  points which intercepts  $n = 12$  at  $p_{\text{tr}}^{\text{extrapolated}} = 345$  MPa (and  $T_{\text{tr}} \approx 440$  K), thus above the limits of our autoclave. An experimental verification of both these predictions, i.e. the appearance of triple points at negative pressures (8CB and 9CB) and at high pressure (12CB), seems extremely interesting.

In order to throw more light on the problem of the strong dependence of the triple point pressure on the length of the alkyl chain, we consider the results of the dielectric relaxation studies of the longest synthesized  $n\text{CB}$ , 14CB, carried out at atmospheric as well as at

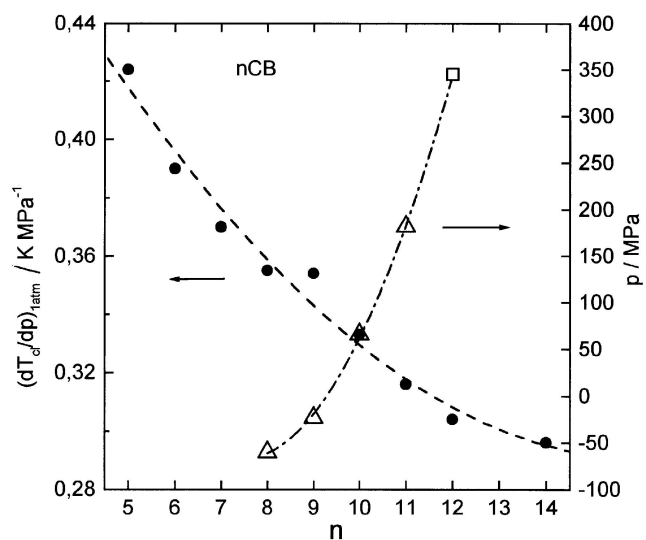


Figure 3. Dependence of the slope of the clearing line (left axis) and the pressure corresponding to the triple point (right axis) on the number of carbon atoms in the alkyl chain for the  $n\text{CB}$  homologous series. Data for 5CB, 6CB, 7CB and 8CB were taken from refs. [22], [23], [23] and [16], respectively. Both lines are exponents fitted to the points.

elevated pressures [15]. The relaxation time characterizing the molecular reorientations around the short axes in the SmA phase, and the derived activation enthalpy and activation volume are very close to those obtained for the much shorter homologue 8CB [19] in the SmA phase. This means that the effective molecular length of 14CB is comparable to that of 8CB in the N and SmA phases. Of course, this is due to the wide range of conformers which can be accessed by such long chains. If so, the molecules become more bulky with increasing  $n$ , and lose their rod-like shapes. Therefore the critical pressure necessary to destroy the smectic layers has to increase with the length of the alkyl chain.

Recently, Mukherjee and Rzoska [20] examined the effect of pressure on the SmA → I phase transition within the framework of the phenomenological Landau theory. They found that: (i) the phase transition is first order even at elevated pressure; (ii)  $T_{\text{cl}}(p)$  is a straight line; (iii) the slope of the clearing line N → I is greater than the slope of the clearing line SmA → I, i.e.

$$dT_{\text{N-I}}/dp > dT_{\text{SmA-I}}/dp. \quad (1)$$

These theoretical predictions are supported, to some extent, by the experimental data. Looking at the DTA traces shown in figure 1, it can be seen that the energy changes accompanying the isotropization of the compounds do not change markedly up to 300 MPa. However, the clearing lines cannot be adequately described by straight lines over a wide pressure range (figure 2); this is due to a decrease of the compressibility

Table 3. Clearing temperature  $T_{cl}$ , the slope of the clearing line  $dT/dp$ , the experimental enthalpy  $\Delta H_{cl}$  and entropy  $\Delta S_{cl}$  of the transition (all at 1 atm), and the volume changes  $\Delta V_{cl}$  as calculated from the Clausius–Clapeyron equation, for members of the *n*CB series.

Substance	Phase transition	$T_{cl}/K$	$dT/dp/K\ MPa^{-1}$	$\Delta H_{cl}/kJ\ mol^{-1}$	$\Delta S_{cl}/J\ mol^{-1}\ K^{-1}$	$\Delta V_{cl}/cm^3\ mol^{-1}$
5CB	I–N	308.3	0.424 [22]	0.33 [22]	1.1	0.45*
6CB	I–N	302.4	0.390 [23]	0.26 [23]	0.9	0.34*
7CB	I–N	315.6	0.370 [23]	0.53 [23]	1.7	0.62*
8CB	I–N	313.8	0.355 [16]	0.50 [16]	1.6	0.57*
9CB	I–N	322.2	0.354	1.63	5.06	1.79
10CB	I–SmA	323.6	0.333	3.05	9.43	3.14
11CB	I–SmA	329.5	0.316	3.85	11.68	3.69
12CB	I–SmA	331.0	0.304	4.57	13.81	4.20
14CB	I–SmA	335.6	0.297	5.72 [15]	17.05	5.06

\* Determined from *pVT* measurements.

of a substance with increasing pressure [21] which was not taken into account in the theory. We can now check whether the inequality (1) has a step-wise character with respect to *n*. In figure 3 (left axis) the slopes determined for all the mesogenic *n*CBs [16, 22, 23] are displayed. It does not appear that either an odd–even alternation or a noticeable step between the nematogenic and smectogenic compounds can be observed. Instead, a rather smooth (exponential) curve describes the dependence of *b* on *n* over the series. Nevertheless, a comparative analysis of the slopes of the clearing lines determined for several two-ring substances with nematic and various smectic phases ( $A_1$ ,  $A_d$ ,  $B_{cr}$ , E) [24] indicates that the inequality (1) seems to be correct. The same conclusion arises from an analysis of the slopes of the clearing lines for 10CB (table 2): the *b*-value for the SmA → I transition is smaller than that for the N → I.

Taking into account the established transition enthalpy,  $\Delta H_{cl}$ , measured using DSC at 1 atm (table 1), the slopes of the clearing lines,  $dT/dp$  (table 2), and the Clausius–Clapeyron equation,  $dp/dT = \Delta H_{cl}/(T_{cl}\Delta V_{cl})$ , one can calculate the entropy change  $\Delta S_{cl} = \Delta H_{cl}/T_{cl}$ , and the volume change  $\Delta V_{cl}$  at the clearing point (at 1 atm). The data quoted in table 3 clearly indicate that the thermodynamic parameters depend on the length of the alkyl chain and are significantly greater for the smectogenic as compared with the purely nematogenic *n*CB compounds.

### 5. Conclusions

The smectogenic 4'-alkyl-4-cyanobiphenyl, like other similar materials exhibiting other smectic polymorphisms [9, 10], transform into the nematic phase under pressure. This seems to indicate that the nematic state is in general favoured with increasing pressure. The pressure corresponding to the triple point increases strongly with the length of the alkyl chain for the *n*CB homologous series. The slope of the clearing temperature,  $dT_{cl}/dp$ , strongly decreases with *n*, but does not show an alternation,

or a step-wise change between the nematogenic and smectogenic members of the series. The thermodynamic parameters characterizing the transition to the isotropic phase clearly depend on the type of the preceding LC phase.

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