

# Spinodal Temperatures at the Nematic to Isotropic Phase Transition from Precise Volumetric Measurements

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High-resolution molar volume data for 4-cyano-4'-*n*-octylbiphenyl (8CB) are presented as a function of temperature near the nematic to isotropic (NI) phase transition. Close to the NI transition the volume was measured at 10 mK temperature steps and at two different pressures. From the data an isobaric thermal expansion coefficient,  $\alpha_p(T)$ , and isothermal compressibility coefficient,  $\beta_T(T)$ , were calculated. Fitting the  $V(T)$  and  $\beta_T(T)$  data according to a tricritical hypothesis with the critical exponents  $\alpha = \alpha' = 1/2$  allowed one to find the spinodal temperatures,  $T^*$  and  $T^{**}$ , on both sides of the first-order phase transition. A universal ratio  $(T_{\text{NI}} - T^*)/(T^{**} - T_{\text{NI}})$  is compared with the theoretical mean field value. The measured volume jump at the transition,  $\Delta V_{\text{NI}}$ , is related to the enthalpy jump,  $\Delta H_{\text{NI}}$ , which was obtained from the very precise calorimetric measurements by other authors.

## I. Introduction

The nematic to isotropic phase transition is the simplest one among the transitions observed between liquid crystalline mesophases. The transition is the most frequently studied theoretically and experimentally. However, the existing thermodynamic data for the transition do not allow judging which of the theoretical models gives the best thermodynamic description. So far the Landau–de Gennes (L-dG) model<sup>1,2</sup> was applied in most of the cases studied. The model assumes an expansion of the free energy in terms of the order parameter,  $Q$ , which for the nematic phase can be written as

$$F(p, T, Q) = F_0(p, T) + \frac{1}{2}a(T)Q^2 - \frac{1}{3}bQ^3 + \frac{1}{4}cQ^4 + \dots - hQ \quad (1)$$

where  $F$  is the molar free energy,  $Q$  is the modulus of the order parameter, the parameter  $a$  is a linear function of temperature, and the last term,  $hQ$ , is field-dependent.

In the nematic phase the long axes of the rodlike molecules are oriented along one direction (with a statistically distributed deviations) while in the isotropic phase they are completely disorganized. The ordering of different phases is characterized by order parameters, and recently Holyst and Oswald<sup>3</sup> summarized their detailed description with definitions. The nematic order parameter,  $Q$ , is in general a tensor variable, which for the uniaxial nematics reduces to

$$Q = \frac{1}{M} \sum_{i=1}^M \left( \frac{3}{2} \cos^2 \theta_i - \frac{1}{2} \right) = \frac{1}{M} \sum_{i=1}^M \langle P_2(\cos^2 \theta_i) \rangle \quad (2)$$

where  $M$  is the number of molecules,  $\theta_i$  is the angle between a long axis of molecule  $i$  and a vector representing the average orientation of the phase (nematic director),  $P_2$  is the second Legendre polynomial, and  $\langle \rangle$  means the statistical ensemble average.

The order–disorder phase transition is always accompanied by broken symmetries; that is, there is no critical point unless a strong external electric or magnetic field is applied.<sup>4,5</sup>

However, Mukherjee<sup>6</sup> claims a theoretical possibility of a critical region (and isolated critical point) at “zero” field, but the symmetry requirements do not allow such a point.<sup>7</sup> If the case of constant pressure and “zero” field is considered, eq 1 is only temperature-dependent by the relation  $a = a't$ , where  $t = (T - T^*)/T_{\text{NI}}$ ,  $T_{\text{NI}}$  is the temperature of the phase transition, and  $T^*$  is the temperature limit of the thermodynamic stability of a supercooled isotropic phase. Equation 1 can be solved for the equilibrium state at  $T_{\text{NI}}$ , for the absolute stability limit of the isotropic phase at  $T^*$ , and for the stability limit of the overheated nematic phase at  $T^{**}$ . Both temperatures,  $T^*$  and  $T^{**}$ , are spinodal temperatures and belong to the spinodal curve having a maximum at the critical (tricritical) point. A detailed solution of eq 1 is given in a very broad theoretical review on the nematic–isotropic phase transition by Gramsbergen et al.<sup>1</sup> It was later discussed in an experimental context by Anisimov<sup>8</sup> and repeated by Mukherjee.<sup>9</sup> The solution allowed us to find the following expressions

$$T_{\text{NI}} = T^* + b^2/27a'c \quad (3)$$

and

$$T^{**} = T^* + b^2/24a'c \quad (4)$$

Equations 3 and 4 allow calculation of the universal ratio

$$(T_{\text{NI}} - T^*)/(T^{**} - T_{\text{NI}}) = 8 \quad (5)$$

Equation 5 is the important result for the later discussion of the results presented here.

In the mean field model described by eq 1 the effective critical exponents  $\alpha$  for the heat capacity and  $\beta$  for the order parameter are equal in the nematic phase,  $\alpha' = \beta = 1/2$  (for  $b \neq 0$ ), while in the isotropic phase both are equal to zero. This simple picture of eq 1 is not compatible with experimental results because the temperature dependence of the heat capacity of the isotropic phase<sup>2,8,10</sup> evidently deviates from a straight line on approaching the transition temperature  $T_{\text{NI}}$ . Also, the exponent for the temperature dependence of the order parameter in the nematic

phase obtained, for example, from the photopyroelectric measurements of thermal conductivity anisotropy<sup>11</sup> and from the dielectric permittivity<sup>12</sup> is very close to  $\beta = 1/4$ . Such a result can be obtained if one extends eq 1 with a sixth order term in  $Q$  and the coefficients  $a$  and  $c$  become simultaneously zero. This would result (for small  $b$ ) near a mean field tricritical point in  $\beta = 1/4$  and  $\alpha = \alpha' = 1/2$ . This assumption of nearly tricritical behavior at the NI transition, suggested earlier by Keyes<sup>13</sup> and Anisimov,<sup>2,14</sup> is analyzed in this paper.

The NI phase transition, however, is considered as very weakly first order, and the weak effect of the transition seems not clear<sup>8</sup> or even “puzzling”.<sup>9</sup> The strength of the transition can be measured by a change of basic thermodynamic properties, like  $\Delta V_{\text{NI}}$  (a volume jump) or  $\Delta H_{\text{NI}}$  (an enthalpy jump) at the phase transition, or by the difference between the spinodal temperatures, which are the temperature limits of thermodynamic stability of a supercooled isotropic phase,  $T^*$ , and an overheated nematic phase,  $T^{**}$ . Spinodal temperatures (or temperatures and concentrations in two-component systems), difficult to find in experiments, are important parameters from a technical point of view. Phase separation during spinodal decomposition, important, for example, in the technology of polymers or polymer-dispersed liquid crystals,<sup>15</sup> occurs beyond the spinodal temperature, while between the binodal and spinodal curves the phase separation occurs through a nucleation mechanism.<sup>16</sup> A similar situation occurs at the phase transition in a pure substance quenched beyond the spinodal or slowly entering the metastable region. The main purpose of this work is the determination of the width of the metastable regions,  $(T^{**} - T_{\text{NI}})$  and  $(T_{\text{NI}} - T^*)$ , at the nematic to isotropic phase transition in 4-cyano-4'-*n*-octylbiphenyl (8CB), as well as the volume jump,  $\Delta V_{\text{NI}}$ . Because of a large number of papers devoted to the NI phase transition and to the compound 8CB, that became a standard liquid crystalline substance, the references cited here are limited to those closely related to the subject of the paper or dealing with the substances of the same homologous series, *n*CB.

The spinodal temperature for the isotropic phase,  $T^*$ , is commonly estimated by the linear extrapolation of the reciprocal temperature dependencies of the intensity of scattered light,<sup>8</sup> the Kerr effect,<sup>17,18</sup> the Cotton–Mouton effect,<sup>4</sup> and the nonlinear dielectric permittivity<sup>19–21</sup> or by fitting the dielectric permittivity<sup>12,20–24</sup> as a function of temperature,  $\epsilon_{\text{iso}}(T - T^*)$ . A much smaller number of papers deal with the spinodal temperature of the nematic phase,  $T^{**}$ . This can be found from the temperature dependencies of the dielectric anisotropy<sup>22</sup>  $\Delta\epsilon(T) = \epsilon_{\parallel} - \epsilon_{\perp}$  ( $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$  are the dielectric permittivities, parallel and perpendicular to the nematic director, respectively) or from the mean value,<sup>12</sup> defined as  $\epsilon_{\text{mean}}(T) = 1/3\epsilon_{\parallel} + 2/3\epsilon_{\perp}$ . Unfortunately, even the precise measurements of dielectric permittivity for 8CB by Thoen and Menu<sup>22</sup> gave the value of  $T^{**}$  equal to the upper limit of the two-phase region. Similar results were obtained by Rzoska et al.<sup>12</sup> for 6OCB and 7OCB. Their values of  $T^{**}$  are even lower than  $T_{\text{NI}}$  for both substances, but the errors of the estimated parameters are quite large (up to  $\pm 0.3$  K), so probably the values of  $T^{**}$  obtained from the fittings fall into the two-phase region, too.

An alternative method of finding the spinodal points,  $T^*$  and  $T^{**}$ , is adiabatic calorimetry.<sup>8,10</sup> Anisimov<sup>8</sup> shows a difference between the values  $\Delta T^* = T_{\text{NI}} - T^*$  obtained from susceptibility and from calorimetric measurements for the substance known as MBBA ( $\Delta T^*_{\text{susc}} = 1\text{--}2$  K;  $\Delta T^*_{\text{cal}} = 0.24$  K), but no explanation of such a discrepancy is given. Similar to the case for  $\Delta T^*_{\text{susc}}$ , results were obtained from the Kerr effect by

Kolinsky and Jennings<sup>18</sup> for the compounds from the *n*CB series ( $n = 6\text{--}9$ ). They found  $\Delta T^*_{\text{KE}} = (1.0\text{--}1.3)$  K for all compounds. The calorimetric data for 8CB were reported by Thoen et al.<sup>10</sup> The authors<sup>10</sup> were able to calculate both spinodal temperatures  $T^*$  and  $T^{**}$ . The value of  $\Delta T^*_{\text{cal}}$  (from calorimetric data) allows one to compare the difference between  $\Delta T^*_{\text{cal}}$  and  $\Delta T^*_{\Delta\epsilon}$  estimated from dielectric anisotropy measured for 8CB (probably for the same sample) by Thoen and Menu.<sup>22</sup> The difference found by Thoen<sup>10,22</sup> is smaller than the one found by Anisimov<sup>8</sup> but still significant, that is,  $\Delta T^*_{\Delta\epsilon} = 1.51$  K and  $\Delta T^*_{\text{cal}} = 0.64$  K. The above numbers are not given explicitly in refs 22 and 10, respectively, but they are necessary for further discussion of our present results. To resolve this evident discrepancy, the thermodynamic values of  $T^*$  and  $T^{**}$  found from the very precise changes of molar volume measured in the close vicinity of the isotropic–nematic transition are presented.

The thermodynamic quantities at the transition are nonanalytical functions of temperature, pressure, or density. Among thermodynamic quantities showing singularities at the phase transition, the thermal dependence of the heat capacity,  $C_p(T)$ , is the one most frequently investigated. The singularity in  $C_p(T)$ , characterized by a critical exponent  $\alpha$ , is usually described with the expression

$$C_p = At^{-\alpha} + B \quad (6)$$

where  $t = |(T - T_c)/T_c|$  is the reduced temperature and  $T_c$  is the temperature corresponding to the singular point (critical or spinodal,  $T^*$  or  $T^{**}$ , for the first-order transition).

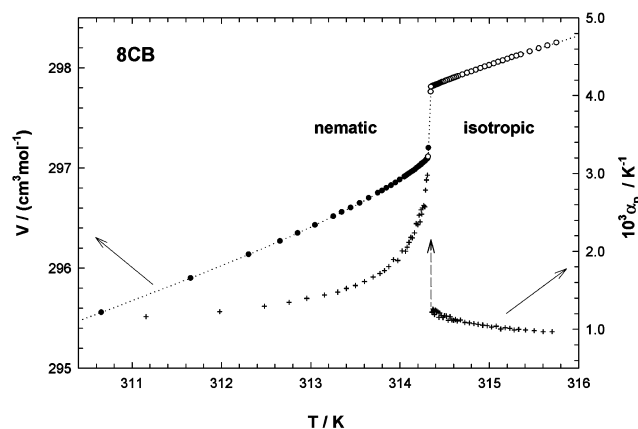
The same functional form is valid for nonanalyticity in the isobaric thermal expansion coefficient,  $\alpha_p(T)$ , and in the isothermal compressibility coefficient,  $\beta_T(T)$ . The above statement can be proved using relations derived by Pippard<sup>25</sup> (and later generalized by Garland<sup>26</sup>) for the singularities at continuous phase transitions. It applies also to the NI phase transition because the spinodal points are singular and they would “meet” at the tricritical point (maximum of a spinodal curve) where the transition becomes continuous. The Pippard equations were recently applied and confirmed experimentally<sup>27</sup> for the singularity at the smectic-A to nematic phase transition.

In the following part of the paper the spinodal temperatures,  $T^*$  and  $T^{**}$ , from the behavior of the molar volume and from the divergence of the compressibility coefficient near the nematic to isotropic phase transition, will be calculated. The volume jump at the transition is also determined with high accuracy. The results are discussed in the context of the mean field theory<sup>1,2</sup> as well as the tricritical hypothesis<sup>13,14</sup> and are related to the calorimetric measurements<sup>10</sup> for the same compound, 4-cyano-4'-*n*-octylbiphenyl (8CB).

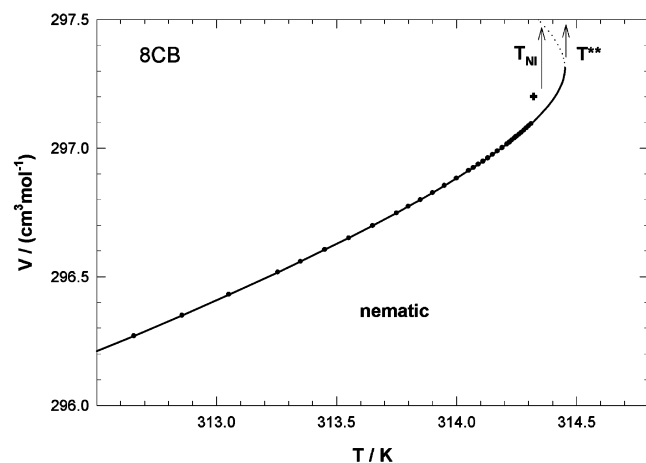
## II. Experiment and Results

The compound, 8CB ( $M = 291.438$  g/mol), used here was synthesized and purified by “ZD Chemipan” (Warsaw, Poland), and further purification by slow fractional crystallization from methanol was done in our laboratory. Thin-layer chromatography of our sample did not reveal any impurities. The sample used in the measurements presented below is the same as the one used in our earlier studies of the smectic-A to nematic phase transition.<sup>27</sup>

The high purity of the sample was confirmed by a very narrow temperature range of the two-phase region at the nematic to isotropic phase transition (below 30 mK; see Figure 3). The temperature at which the first drop of the nematic phase appears



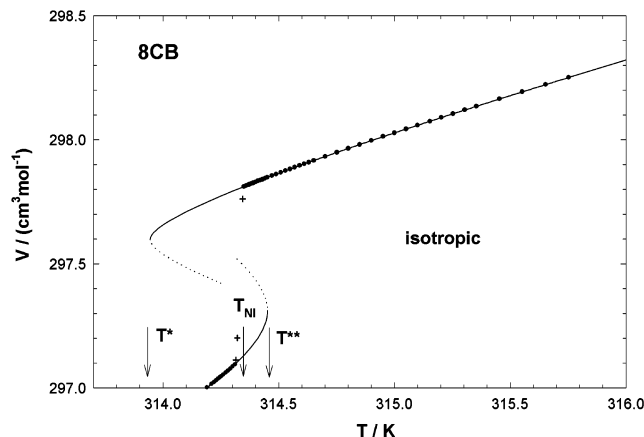
**Figure 1.** Molar volume and thermal expansion coefficient near the nematic to isotropic phase transition in 8CB: (●) volume measured in the nematic phase during heating; (○) volume measured in the isotropic phase during cooling; (+) thermal expansion coefficient calculated from the neighboring data points according to eq 7.



**Figure 2.** Molar volume changes with temperature for the nematic phase on approaching the NI transition: (●) points measured in the heating run; (+) first point in the two-phase region measured on heating; (—) calculated from eq 8 with the parameters from the fit 4 in Table 1 and extrapolated to the spinodal temperature  $T^{**}$ ; (···) further extrapolation to an unstable region.

on cooling was taken as the transition temperature,  $T_{NI} = 314.345$  K. A detailed description of the equipment and the measuring procedure was given in our earlier paper.<sup>28</sup> The experimental setup allows for the measurements of volume as a function of temperature in steps of  $\sim 10$  mK and simultaneously as a function of pressure in a very narrow (up to 2 bar) pressure range. The glass dilatometer with a pressure jacket and an assembly of manometers was successfully applied for studies of extremely weak phase transitions, for example, smectic-C to smectic-A.<sup>28,29</sup> It should be mentioned that in the present experiment the size of the sample was smaller, about 5.6 cm<sup>3</sup> (a bigger volume of mercury was added to fill the dilatometer), to allow us to cover the temperature range  $\sim 2$  K in one series of measurements, that is, without removing the mercury. The temperature of a 70 dm<sup>3</sup> water bath was controlled with a precision of  $\pm 0.2$  mK, and the resolution of the volume measurements was  $\sim 0.1$  ppm. A pressure jacket around a container of the dilatometer allowed one to keep approximately equal pressures inside and outside the container to avoid errors caused by glass elasticity. Corrections for the small pressure differences were made, as described in ref 28.

**A. Molar Volume and Thermal Expansion.** The results of the volumetric measurements are presented in Figure 1 as a



**Figure 3.** Molar volume changes with temperature for the isotropic phase in the vicinity of the transition to the nematic phase: (●) points measured in the cooling run; (+) the three points in the two-phase region; (—) calculated from eq 8 with parameters from fit 1 in Table 1 and extrapolated to the spinodal temperature  $T^{*}$ ; (···) further extrapolation to an unstable region;  $T_{NI}$  is the transition temperature; part of the curve for the nematic phase from Figure 2 is also shown.

temperature dependence of molar volume at  $p = 1.013$  bar. Also shown are the average values of the thermal expansion coefficient, calculated as

$$\bar{\alpha}_p = \bar{V}^{-1}(\Delta V / \Delta T)_p \quad (7)$$

from the pairs of neighboring data points. It occurred that the mean values of  $\bar{\alpha}_p$  are too scattered for the numerical analysis, especially when the points are measured at rather small temperature steps, that is, 10 mK. Therefore, eq 6 as applied for  $\alpha_p$  was integrated and used to describe the direct results of molar volume as a function of temperature

$$V_T(T) = \begin{cases} At^{(1-\alpha)} + Bt + C & T > T_{NI} \\ A't^{(1-\alpha')} + B't + C' & T < T_{NI} \end{cases} \quad (8)$$

where  $t = |(T - T_{sp})/T_{sp}|$  is the reduced temperature, the exponent  $\alpha = \alpha' = 1/2$ , and  $T_{sp}$  is the spinodal temperature, which is equal to  $T^{*}$  for  $T > T_{NI}$  and  $T^{**}$  for  $T < T_{NI}$ .

The above equations have the same form as the equations used by other authors<sup>12,19–24</sup> to describe the temperature dependence of the dielectric permittivity. The critical exponents  $\alpha$  and  $\alpha'$  were fixed at the values  $\alpha = \alpha' = 1/2$ , according to the tricritical hypothesis<sup>13,14</sup> confirmed by the results of many experiments.<sup>10–12,19–24</sup> It has to be mentioned here that the critical exponents  $\alpha = \alpha' = 0.11$ , classifying the system in the Ising universality class<sup>30</sup> ( $d = 3$ ,  $n = 1$ ), were also checked. The fit for  $T > T_{NI}$  was slightly worse than that with  $\alpha = 1/2$  and resulted in  $(T^{*})_{\alpha=0.11} > (T^{*})_{\alpha=1/2}$ , but for  $T < T_{NI}$  a nonlinear least squares procedure could not reach a convergence and always stopped at the constraint  $T^{**} > T_{NI}$ , giving nonrandom and very high deviations. Thus, the results of those fits are not included in the paper.

We measured approximately 80 values of  $V(T)$  within the temperature range 312.3–315.8 K. Below  $T = 312$  K a pretransitional effect of the nematic to smectic-A transition is visible (the sign of the curvature changes), and the inclusion of the points from that range causes systematic deviations, so the standard deviation of the fits increases dramatically. Equations 8 were used in the fitting procedure with range shrinking to prove that the resulting parameters do not depend on the fitted

**TABLE 1: Parameter Values Obtained from the Fitting of Molar Volume Data with Eqs 8 for 8CB above and below the Nematic to Isotropic Phase Transition<sup>a</sup>**

Isotropic Phase								
fit	<i>n</i>	<i>T</i> <sub>max</sub> <sup>b</sup>	<i>A</i> (cm <sup>3</sup> /mol)	<i>B</i> (cm <sup>3</sup> /mol)	<i>C</i> (cm <sup>3</sup> /mol)	<i>T</i> <sup>*</sup> (K)	<i>T</i> <sub>NI</sub> − <i>T</i> <sup>*</sup> (K)	10 <sup>4</sup> σ (cm <sup>3</sup> /mol)
1	42	315.7534	3.5619 ±0.0999	66.4812 ±0.6338	297.5977 ±0.0082	313.9446 ±0.0147	0.400	1.0
2	33	315.1002	3.2595 ±0.3359	68.7934 ±2.4776	297.6179 ±0.0237	313.9783 ±0.0403	0.367	1.0
3	24	314.6516	3.5636 ±2.0742	64.2965 ±17.8960	297.6179 ±0.1141	313.9923 ±0.1711	0.353	0.9
Nematic Phase								
fit	<i>n</i> '	<i>T</i> <sub>min</sub> <sup>c</sup>	<i>A</i> ' (cm <sup>3</sup> /mol)	<i>B</i> ' (cm <sup>3</sup> /mol)	<i>C</i> ' (cm <sup>3</sup> /mol)	<i>T</i> <sup>**</sup> (K)	<i>T</i> <sup>**</sup> − <i>T</i> <sub>NI</sub> (K)	10 <sup>4</sup> σ (cm <sup>3</sup> /mol)
4	36	312.3070	−8.8984 ±0.0516	−64.9499 ±0.3620	297.3147 ±0.0028	314.4548 ±0.0023	0.110	1.8
5	32	313.2548	−8.8084 ±0.1137	−65.6896 ±0.9536	297.3108 ±0.0052	314.4520 ±0.0039	0.107	1.7
6	21	314.0503	−8.9601 ±1.4884	−63.0700 ±17.1498	297.3132 ±0.0496	314.4524 ±0.0308	0.107	1.6

<sup>a</sup> *T*<sub>NI</sub> = 314.345 K; σ is the standard deviation of the fits. <sup>b</sup> In the isotropic phase *T*<sub>min</sub> = 314.3496 K and *T*<sub>max</sub> determine the fitted temperature range; *n* is the number of points in this range. <sup>c</sup> In the nematic phase *T*<sub>min</sub> and *T*<sub>max</sub> = 314.3108 K determine the fitted temperature range; *n*' is the number of points in this range.

temperature range. The parameters of the six most representative fits are collected in Table 1. The quality of all fits is represented by the standard deviation, σ, and by the weighted value  $\chi_v^2$ , defined as

$$\chi_v^2 = \frac{1}{n-p} \sum_{i=1}^n w_i (X_i^{\text{expt}} - X_i^{\text{calc}})^2 \quad (9)$$

where *X*<sub>*i*</sub> is replaced by *V*<sub>*i*</sub> or β<sub>*T*</sub>, *w*<sub>*i*</sub> is the weight of each point, *n* is the number of experimental points, and *p* is the number of adjustable parameters.

The calculations were carried out twice: for *w*<sub>*i*</sub> = 1 (then  $\chi_v^2$  is the square of standard deviation of the fit,  $\chi_v^2 = \sigma$ ) and for *w*<sub>*i*</sub> = 1/σ<sub>*i*</sub><sup>2</sup>, where σ<sub>*i*</sub><sup>2</sup> = σ<sub>*X*</sub><sup>2</sup> + σ<sub>*T*</sub><sup>2</sup>(d*X*/d*T*)<sup>2</sup> with σ<sub>*X*</sub> being an experimental error of *V* or β<sub>*T*</sub> and σ<sub>*T*</sub> = 0.0002 K. For a correct error estimation and a quality of the fit corresponding to the experimental error, the  $\chi_v^2$  value should converge to unity. The  $\chi_v^2$  values are not included in the tables, but with the estimated errors σ<sub>*T*</sub> = 0.0002 K, σ<sub>*V*</sub> = 0.0002 cm<sup>3</sup>/mol, and σ<sub>*β*</sub> = 0.4 × 10<sup>−6</sup> bar<sup>−1</sup> (~0.5%), the values  $\chi_v^2 \cong 0.8$ –1.5 were usually obtained.

It can be seen from Table 1 that the standard deviations of the fits for the nematic phase are approximately 2 times greater than those for the isotropic phase, although the scattering of the deviations is perfectly random in all cases. We explain that by a higher viscosity of the nematic phase (approximately by a factor of 5) and small density gradients caused by blocked relaxation during expansion. The expanding liquid (during heating) in the dilatometer must push up a mercury column (up to 370 mm high) in a thin capillary (0.3 mm diameter), and a state of thermal equilibrium is reached through some temperature oscillations, although very small (see ref 28 for technical details). The greatest standard deviation of the fits is equal to 1.8 × 10<sup>−4</sup> cm<sup>3</sup>/mol, which is equivalent to 0.6 ppm and is comparable with the estimated experimental error, ~0.3 ppm.

The results of the fits are depicted in Figures 2 and 3, for the nematic and isotropic phases, respectively. The deviations of particular points from the fitted curves (calculated with the parameters of fits 1 and 4 in Table 1) are not visible because they are smaller than the resolution of the volume scale by 2 orders of magnitude and are therefore even smaller than the

thickness of the line. The same temperature and volume ranges are shown for both phases in these figures to preserve the same scale resolution for comparison. The calculated curves are extrapolated to the spinodal temperatures (marked with arrows) and to an unstable region. Fits 1–3 show that *T*<sup>\*</sup> slightly depends on range shrinking, and the difference, Δ*T*<sup>\*</sup> = *T*<sub>NI</sub> − *T*<sup>\*</sup>, is getting smaller when the points far from the transition are excluded; Δ*T*<sup>\*</sup> ranges from 0.35 to 0.40 K. The values of *T*<sup>\*\*</sup> are more stable and the average value equals *T*<sup>\*\*</sup> = (314.453 ± 0.003) K, so Δ*T*<sup>\*\*</sup> = *T*<sup>\*\*</sup> − *T*<sub>NI</sub> = (0.108 ± 0.003) K. The calculated ratio (*T*<sub>NI</sub> − *T*<sup>\*</sup>)/(*T*<sup>\*\*</sup> − *T*<sub>NI</sub>) = 3.3–3.7 and differs significantly from the theoretical ratio, which is equal to 8 (see eq 5). The possible reasons for such a discrepancy will be discussed in section III.

An advantage of our direct volumetric measurements is that we are able to find the precise value of the volume change, Δ*V*<sub>NI</sub>, at the phase transition, which is as important as the latent heat, Δ*H*<sub>NI</sub>, measured directly by adiabatic calorimetry.<sup>10</sup> Substituting *T*<sub>NI</sub> for *T* in eqs 8, we calculated the volumes of both phases at the NI transition. The results *V*(*T*<sub>NI</sub><sup>+</sup>) = 297.8097 cm<sup>3</sup>/mol and *V*(*T*<sub>NI</sub><sup>−</sup>) = 297.1257 cm<sup>3</sup>/mol for the isotropic and nematic phases, respectively, give the minimum value of Δ*T*<sub>NI</sub><sup>min</sup> = 0.684 cm<sup>3</sup>/mol (Δ*T*<sub>NI</sub><sup>min</sup>/*V*<sub>NI</sub> = 2.30 × 10<sup>−3</sup>). The value estimated as a difference of the volumes measured at the limits of the two-phase region, Δ*T*<sub>NI</sub><sup>max</sup> = 0.716 cm<sup>3</sup>/mol, determines an upper limit of the volume change at the transition because of a strong pretransitional increase of volume in the temperature range Δ*T*<sub>NI</sub> = 24 mK, which corresponds to the two-phase region. In further discussion in section III the value Δ*T*<sub>NI</sub><sup>min</sup> will be considered as the more reliable one.

The isobaric thermal expansion coefficient α<sub>*p*</sub> = *V*<sup>−1</sup>(d*V*/d*T*)<sub>*p*</sub> was calculated by an analytical differentiation of eqs 8, which gave the equations below, equivalent to eqs 6:

$$\alpha_p(T) = \begin{cases} \frac{1}{V(T)T_{sp}}[(1 - \alpha)At^{-\alpha'} + B] & T > T_{NI} \\ \frac{-1}{V(T)T_{sp}}[(1 - \alpha')A't^{-\alpha'} + B'] & T < T_{NI} \end{cases} \quad (10)$$

with α = α' = 1/2, as previously justified.

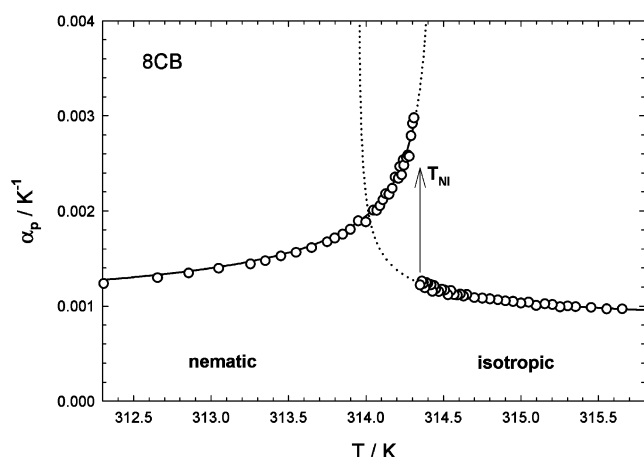
The thermal dependence of α<sub>*p*</sub>(*T*), calculated according to eqs 10 with the parameters of fits 1 and 4 (Table 1) with curves



**TABLE 2: Parameter Values Obtained from the Fitting of the Compressibility Coefficient,  $\beta_T(T)$ , with Eqs 12 for 8CB above and below the Nematic to Isotropic Phase Transition<sup>a</sup>**

Isotropic Phase							
fit	$n$	$T_{\max}^b$ (K)	$A$ ( $10^{-6}$ bar $^{-1}$ )	$B$ ( $10^{-6}$ bar $^{-1}$ )	$T^*$ (K)	$T_{\text{NI}} - T^*$ (K)	$10^4\sigma$ ( $10^{-6}$ bar $^{-1}$ )
1	41	315.7534	0.6138 $\pm 0.0567$	63.82 $\pm 0.84$	314.0511 $\pm 0.0317$	0.308	0.43
2	32	315.1002	0.5077 $\pm 0.0815$	65.66 $\pm 1.44$	314.1048 $\pm 0.0405$	0.254	0.47
3	23	314.6516	0.3729 $\pm 0.1541$	68.44 $\pm 3.44$	314.1679 $\pm 0.0651$	0.191	0.50
Nematic Phase							
fit	$n'$	$T_{\min}^c$ (K)	$A'$ ( $10^{-6}$ bar $^{-1}$ )	$B'$ ( $10^{-6}$ bar $^{-1}$ )	$T^{**}$ (K)	$T^{**} - T_{\text{NI}}$ (K)	$10^4\sigma$ ( $10^{-6}$ bar $^{-1}$ )
4	32	312.6561	1.8415 $\pm 0.0567$	59.75 $\pm 0.84$	314.4569 $\pm 0.0317$	0.102	0.52
5	29	315.7534	1.8910 $\pm 0.0410$	59.02 $\pm 0.68$	314.4652 $\pm 0.0062$	0.106	0.45
6	22	313.6499	1.7549 $\pm 0.0714$	61.83 $\pm 1.43$	314.4507 $\pm 0.0093$	0.092	0.43

<sup>a</sup>  $T_{\text{NI}}(p = 1.4 \text{ bar}) = 314.359 \text{ K}$ ;  $\sigma$  is the standard deviation of the fits. <sup>b</sup> In the isotropic phase  $T_{\min} = 314.3496 \text{ K}$  and  $T_{\max}$  determine the fitted temperature range;  $n$  is the number of points in this range. <sup>c</sup> In the nematic phase  $T_{\min}$  and  $T_{\max} = 314.3010 \text{ K}$  determine the fitted temperature range;  $n'$  is the number of points in this range.



**Figure 4.** Thermal expansion coefficient,  $\alpha_p$ , near the nematic to isotropic phase transition: (O) results calculated from pairs of neighboring data points according to eq 7; (•) calculated from eqs 10 with parameters from Table 1 (fits 1 and 4 for the isotropic and nematic phases, respectively); (---) denotes the metastable region.

$\alpha_p(T)$ , are presented in Figure 4 along with the  $\bar{\alpha}_p$  values obtained as numerical derivatives according to eq 7.

**B. Compressibility Coefficient.** From measurements of the volume at constant temperature and at two pressures ( $\sim 1.0$  and  $1.8 \text{ bar}$ ), we get directly the isothermal compressibility coefficient, calculated as

$$\beta_T = -\frac{1}{\bar{V}} \left( \frac{\Delta V}{\Delta p} \right)_T \quad (11)$$

where  $\bar{V}$  is the mean value of volumes measured at two different pressures.

A pressure difference  $\Delta p \leq 0.8 \text{ bar}$ , which, in the case of liquids of low compressibility, can be considered as a differential increment,  $dp$ , allows us to make very precise measurements of the isothermal compressibility coefficient,  $\beta_T$ . Small increments of pressure allow us to measure  $\beta_T$  very close to the transition temperature. Close to the transition temperature the measurements were taken at temperature increments of  $10 \text{ mK}$ .

The temperature dependence of the isothermal compressibility coefficient,  $\beta_T(T)$ , calculated according to eq 11, was fitted to

eqs 12, identical to eq 6 for  $C_p$ ,

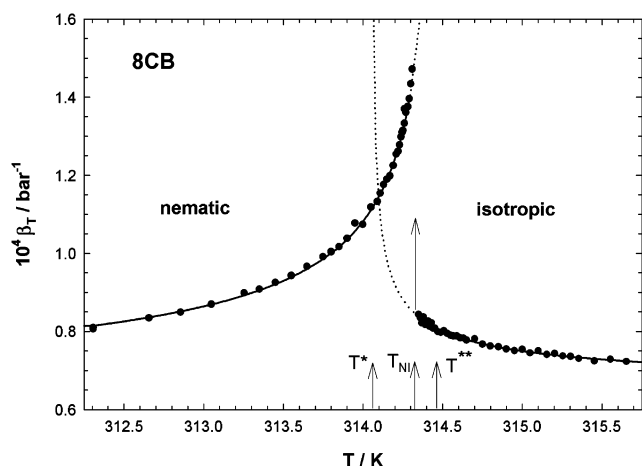
$$\beta_T(T) = \begin{cases} At^{-1/2} + B & T > T_{\text{NI}} \\ A't^{-1/2} + B' & T < T_{\text{NI}} \end{cases} \quad (12)$$

where  $t = |(T - T_{\text{sp}})/T_{\text{sp}}|$  is the reduced temperature and  $T_{\text{sp}}$  is the spinodal temperature equal to  $T^*$  and  $T^{**}$  for  $T > T_{\text{NI}}$  and  $T < T_{\text{NI}}$ , respectively.

The results of the fits with range shrinking, as it was done for  $V(T)$  analysis, are presented in Table 2. The standard deviations of the fits correspond to an error of  $\sim 0.5\%$ . The spinodal temperatures, found as adjustable parameters, are somewhat higher than those found from  $V(T)$  curves. It has to be noticed that the  $\beta_T(T)$  values were measured at an average pressure  $0.4 \text{ bar}$  higher than that for the  $V(T)$  values. So, the NI transition temperature had to be corrected by  $14 \text{ mK}$ , taking into account that  $(dp/dT)_{\text{NI}} \cong 29 \text{ bar/K}$  (this value will be discussed in section III). The correction gave the transition temperature  $T_{\text{NI}}(p = 1.4 \text{ bar}) = 314.359 \text{ K}$ , and this value was used to calculate the differences  $\Delta T_{\beta}^* = T_{\text{NI}}(1.4 \text{ bar}) - T_{\beta}^*$  and  $\Delta T_{\beta}^{**} = T_{\text{NI}}(1.4 \text{ bar}) - T_{\beta}^{**}$  for the isotropic and nematic phases, respectively. The resulting values are also given in Table 2. The spinodal temperatures,  $T_{\beta}^*$ , as well as the other parameters calculated from the side of the isotropic phase are slightly sensitive to range shrinking, which suggests that the points closer to the transition are too high and removing the points far from the transition increases the statistic weight of the former ones, which results in higher  $T_{\beta}^*$  and smaller  $\Delta T_{\beta}^*$ . The values of  $\Delta T_{\beta}^*$  in Table 2 are also a little smaller than  $\Delta T_{\beta}^*$  in Table 1, so in further discussion more attention will be paid to the results of direct volumetric measurements as the most reliable. The results from the side of the nematic phase (especially fits 4 and 5 in Table 2) are independent of the fitted temperature range and are approximately the same as those obtained from the volumetric measurements, which increases the reliability of the data. The curves calculated from fits 1 and 4 in Table 2 (whole measured temperature range) are depicted in Figure 5 together with the particular values of the isothermal compressibility coefficient,  $\beta_T$ , calculated according to eq 11.

### III. Discussion and Conclusions

The first volumetric measurements at the NI phase transition for 8CB were reported by Leadbetter et al.<sup>31</sup> in 1977. Unfor-



**Figure 5.** Isothermal compressibility coefficients,  $\beta_T$ , versus temperature in the vicinity of the nematic to isotropic phase transition: (●) points calculated from eq 11; (—) calculated from eqs 12 with parameters from Table 2 (fits 1 and 4 for the isotropic and nematic phases, respectively); (⋮) denotes the metastable region.

Unfortunately, the measurements were not precise enough for any quantitative analysis and the measured volume jump  $\Delta V_{NI} = (0.95 \pm 0.15) \text{ cm}^3/\text{mol}$  exceeds our value by about 30%. Since then many papers dealing with volumetric measurements were published, but the authors were not interested in determination of spinodals. Moreover, the precision of their data did not allow it, anyway. Sandman and Wurflinger<sup>32</sup> reported a good thermodynamic description of the transition based on  $pVT$  measurements, that is, on 14 isotherms  $V(p)$ , but they also did not try to estimate a pressure at which the mechanical stability of the nematic phase finally breaks, that is, the spinodal pressure. In the isotropic phase the  $V(p)$  curves are “bent-up”, so there is no evidence of any spinodal. The authors<sup>32</sup> made a comparison with the other measurements of  $\Delta V_{NI}$ , showing significant differences. The value given by Leadbetter et al.<sup>31</sup> is the greatest one ( $\Delta V_{NI}/V_{NI} = 0.32\%$ ), and that given by Dunmur and Miller<sup>33</sup> is the smallest one ( $\Delta V_{NI}/V_{NI} = 0.165\%$ ). The result from  $pVT$  measurements by Shirakawa et al.<sup>34</sup> is in very good agreement with our value  $\Delta V_{NI}/V_{NI} = 2.30 \times 10^{-3}$ . They report the value  $\Delta V_{NI}/V_{NI} = 0.23\%$  and also the transition temperature  $T_{NI} = 313.84 \text{ K}$ , which is the closest to our  $T_{NI} = 314.345 \text{ K}$  (the other reported transition temperatures are lower).

The most reliable and detailed thermal study of the NI transition in 8CB was made by Thoen et al.<sup>10</sup> using an adiabatic scanning calorimeter of very high resolution. They found that a discontinuity in enthalpy at the NI phase transition is  $\Delta H_{NI} = (614 \pm 5) \text{ J/mol}$ . This value can be related to our  $\Delta V_{NI} = (0.684 \pm 0.008) \text{ cm}^3/\text{mol}$  by the Clapeyron equation

$$(dp/dT)_{NI} = \Delta H_{NI}/T\Delta V_{NI} \quad (13)$$

where  $(dp/dT)_{NI}$  is the slope of the nematic–isotropic coexistence line.

It should be mentioned that the error in our estimation  $\delta V = \pm 0.008 \text{ cm}^3/\text{mol}$  comes from uncertainty in the fitting parameter  $C$  (Table 1, fit 1) but not from the error of volume measurements, which is 20 times smaller. The calculated value  $(dp/dT)_{NI} = (28.6 \pm 0.6) \text{ bar/K}$ , from eq 13, with an overestimated error, falls in the range between the value  $27.8 \text{ bar/K}$  reported by Shashidhar and Venkatesh<sup>35</sup> and the value  $31 \text{ bar/K}$  obtained by Shirakawa et al.,<sup>34</sup> but it agrees very well with the value  $29 \text{ bar/K}$  estimated from a phase diagram given by Kasting et al.<sup>36</sup> The three thermodynamic quantities related by eq 13 and coming

from different authors are very consistent, giving a proof of their correctness and accuracy.

The spinodal temperatures reported here, or rather the differences  $(T_{NI} - T^*) = (0.38 \pm 0.04) \text{ K}$  and  $(T^{**} - T_{NI}) = (0.108 \pm 0.003) \text{ K}$ , are also in very good agreement with the results reported by Thoen et al.<sup>10</sup> We compare our results only to that obtained by Thoen et al.<sup>10</sup> from the fits with exponent  $\alpha = 1/2$  (see Table 5 in ref 10). The fit in the isotropic phase<sup>10</sup> (fit 2 in Table 5) shows the highest standard deviation among the others, so the reported  $\Delta T_{cal}^* = 0.64 \text{ K}$  might contain some error, but it is still closer to our value than to a very different  $\Delta T_{\Delta\epsilon}^* > 1 \text{ K}$ , as usually determined from dielectric measurements.<sup>12,20–24</sup> The differences of  $\Delta T_V^*$  and  $\Delta T_{cal}^*$ , as obtained from volumetric and calorimetric measurements, should be equal according to well-known thermodynamic relations, for example, Pippard equations,<sup>25,26</sup> but they might be different from  $\Delta T_{\Delta\epsilon}^*$  because of different crossover ranges for these physical quantities. This discrepancy might also suggest that the density fluctuations in the isotropic phase appear earlier and are stronger than the pretransitional orientational ordering. The evidence of strong pretransitional effects in  $V(T)$ , confirmed also by compressibility data  $\beta_T(T)$ , shows the breakdown of mechanical stability of the isotropic phase, not predicted by any mean field theory.

A situation, when the mechanical stability of the nematic phase breaks down earlier than its orientational stability, was found theoretically (in the mean field lattice model)<sup>37</sup> and later mentioned by Van Hecke and Stecki.<sup>38</sup> Unfortunately, on the side of the nematic phase the experimental situation is not clear. From the dielectric measurements the values  $T_{\epsilon}^{**} \leq T_{NI}$  were obtained,<sup>12,22</sup> so the only explanation of that fact is experimental error (probably a wide two-phase region). On the contrary, the volumetric measurements (fits 4–6 in Table 1) give the difference  $\Delta T_V^{**} = (T^{**} - T_{NI}) = (0.108 \pm 0.003) \text{ K}$ , in perfect agreement with  $\Delta T_{\beta}^{**} = (0.104 \pm 0.006) \text{ K}$  found from fitting the compressibility coefficients (fits 4 and 5 in Table 2). Also, the value  $\Delta T_{cal}^{**} = 0.11 \text{ K}$  from adiabatic calorimetry reported by Thoen et al.<sup>10</sup> (fit 5 in Table 5) remains in perfect agreement with our results.

In conclusion, the data  $\Delta V_{NI}$ ,  $\Delta T^*$ , and  $\Delta T^{**}$  presented here show that the nematic to isotropic phase transition is much weaker than that predicted by the L-dG model<sup>1</sup> and closer to that predicted by the tricritical hypothesis.<sup>13,14</sup> Anyway, the volume jump and the difference of spinodal temperatures, being the measure of the transition strength, can be measured with good accuracy. The smaller than expected  $\Delta V_{NI}$  can be explained by biaxiality of the molecules, as shown by Holyst and Poniewierski.<sup>39</sup> Earlier, Gelbart and Barboy<sup>40</sup> gave a rough estimate that even small biaxiality of the molecules can reduce a density jump by a factor of 10. The discrepancy between the theoretical and experimental values of  $(T_{NI} - T^*)$  was explained by Mukhopadhyay and Mukherjee,<sup>41</sup> who introduced into the model a coupling of the order parameter with density. Including the density dependence of the three parameters in eq 1, the authors<sup>41</sup> obtained  $T_{NI} - T^* \cong 1 \text{ K}$  and reasonable values of such thermodynamic quantities as  $(dT/dp)_{NI}$ ,  $(dQ/dT)_{NI}$ , and the compressibility coefficient. The density effects can also explain the smaller experimental ratio  $(T_{NI} - T^*)/(T^{**} - T_{NI}) = 3.3–3.7$ , which is supposed to be universal, but according to the L-dG model, it should be equal to 8. The low value of  $T^{**} - T^* = (0.49 \pm 0.04) \text{ K}$  strongly supports the nearly tricritical character of the nematic to isotropic phase transition. The results presented here are the most precise measurements of  $\Delta V_{NI}$ ,  $\beta_T$ ,

$T_{\text{NI}} - T^*$ , and  $T^{**} - T_{\text{NI}}$  and therefore can be used as a standard reference for further theoretical and experimental verification.

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