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On the temperature dependence of the order parameter of liquid crystals over a wide nematic range

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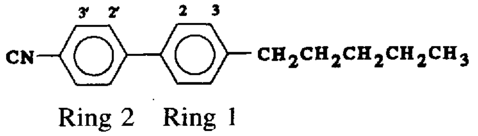
Based on the ideas of Landau–de Gennes theory applied to nematic liquid crystals, several forms for the variation of the order parameter as a function of temperature are investigated over a wide nematic range. These functional forms are used to fit the experimental order parameters, determined through the use of C-13 NMR, for 4-methoxybenzylidene-4′-butylaniline (MBBA) and 4-*n*-pentyl-4′-cyanobiphenyl (5CB), and the physical significance of the parameters is discussed. A comparison of the results shows that the functional form which fits the experimental data best is similar to the Haller equation, a useful relation which is usually regarded as empirical. In this case, the coefficients resulting from a semi-empirical approach based on the Landau–de Gennes treatment may be thought of as quantifying the importance of the structure and rigidity of the liquid crystal in determining the temperature dependence of the order parameter for that liquid crystal. In the process, we have also examined the pretransitional behaviour in the C-13 NMR chemical shifts of liquid crystals observed within a few tenths of a degree above the nematic to isotropic transition temperature.

1. Introduction

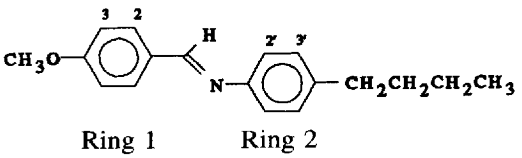
Many interesting properties and important applications of nematic liquid crystals result from their anisotropic orientational ordering, which can be quantified through the use of the order parameter. The variation of the order parameter as a function of temperature has been the subject of much interest, and several approaches have been used to describe the temperature dependence of the order parameter. For example, the Maier–Saupe mean-field theory [1, 2] predicts that the order parameter of nematic liquid crystals is a universal function of temperature, which is not observed experimentally. Other variations of mean-field theory do allow for differences between liquid crystals, but do not always predict experimentally observed results [3]. The Landau–de Gennes theory has also been used to derive the temperature dependence of the order parameter from a low-order polynomial which approximates the free energy density of the nematic liquid crystal [4, 5]. A third approach is to use empirical relations to describe the order parameter as a function of temperature. The most widely used [6–11] empirical relation is probably the Haller relation [12].

In the present work, we will derive several other relationships between the order parameter and temperature based on Landau–de Gennes theory and show that one of the semi-empirical relations can be simplified to the Haller equation. These expressions will be compared with the experimental results for 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) and 4-*n*-pentyl-4′-cyanobiphenyl (5CB).

5CB



MBBA



The order parameters for both rings were determined by C-13 nuclear magnetic resonance (NMR) spectroscopy, combining the SLF/VAS (separated local field spec-

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troscopy/variable angle spinning) technique with chemical shift data [9, 11, 13–16]. Because the C-13 chemical shifts can be measured accurately as a function of temperature, it is possible to obtain a precise determination of the order parameter for a large number of temperatures. This increases the reliability of the comparison between the experimental and derived results.

In the isotropic phase, when the chemical shifts are measured a few tenths of a degree above the isotropic to nematic transition temperature, they deviate from their values at higher temperatures, and this can be attributed to the pretransitional behaviour [17]. This deviation can be described in terms of local fluctuations of the ordering tensor.

2. Experimental

MBBA was purchased from Aldrich Chemical and recrystallized three times from cold ethanol. The nematic to isotropic transition temperature, 47·0°C, determined by the use of an Olympus BH-2 polarizing microscope equipped with a Linkham PR600 heating stage, agrees well with literature values. The observed isotropic to nematic transition is very sharp, indicating a high purity, which is confirmed by the proton NMR spectrum of the sample dissolved in deuterated chloroform. 5CB, which is more stable than MBBA, was obtained from EM Chemicals, Hawthorne, New York, and was used without purification. The nematic range of 5CB specified by the supplier was 23·0–35·3°C.

The order parameters were measured on a Varian XL-300 NMR spectrometer equipped with a variable angle spinning probe manufactured by Doty Scientific, Columbia, South Carolina. The C-13 chemical shifts of the liquid crystals were measured on a Varian VXR-500S spectrometer with an indirect detection probe manufactured by Nalorac Cryogenics Corporation, Martinez, California, which allows a high degree of temperature control (± 0·1 K) for the liquid crystal samples.

3. Results and discussion

In this section, we will first briefly review some of the ideas developed in the Landau–de Gennes theory of nematic liquid crystals and then derive several equations for the variation in the order parameter as a function of temperature. A comparison between the expressions resulting from these derivations and experimental data will be given in the last part of this section.

3.1. *Basic expressions of order parameter and transition enthalpy*

According to Landau–de Gennes [4, 5], the Helmholtz free energy density, f_N, of a nematic liquid crystal phase at constant density can be expressed in terms of a polynomial expansion of **Q**, the symmetric tensor order parameter.

$$f_N = f_I + \tfrac{1}{2}A_{\alpha\beta\gamma\delta}Q_{\alpha\beta}Q_{\gamma\delta} - \tfrac{1}{3}B_{\alpha\beta\gamma\delta\mu\nu}Q_{\alpha\beta}Q_{\gamma\delta}Q_{\mu\nu} + \tfrac{1}{4}C_{\alpha\beta\gamma\delta\mu\nu\psi\sigma}Q_{\alpha\beta}Q_{\gamma\delta}Q_{\mu\nu}Q_{\psi\sigma} + \dots \qquad (1)$$

f_N is the Helmholtz free energy density of the isotropic phase, and A, B, and C are coefficients of the tensor elements and are dependent on temperature and pressure. In principle, the expansion may be of arbitrarily high order, but the mathematics becomes complex. If we limit the expansion to the terms shown and consider the liquid crystal to be uniaxial, symmetry considerations simplify equation (1) to

$$f_N = f_I + \tfrac{1}{2}AQ_{\alpha\beta}Q_{\beta\alpha} - \tfrac{1}{3}BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \tfrac{1}{4}C(Q_{\alpha\beta}Q_{\beta\alpha})^2 \qquad (2)$$

For a uniaxial nematic, the tensor order parameter may be expressed as

$$Q_{\alpha\beta} + S(N_{\alpha\beta} - \tfrac{1}{3}\delta_{\alpha\beta}) \qquad (3)$$

where S is the conventional orientational order parameter, and **N** and $\boldsymbol{\delta}$ are tensors which relate **Q** to S. The following relations emerge from equation (3):

$$Q_{\alpha\beta}Q_{\beta\alpha} = \tfrac{2}{3}S^2 \qquad (4)$$

and

$$Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} = \tfrac{2}{9}S^3. \qquad (5)$$

Thus, f_N may be expressed as

$$f_N = f_I + \tfrac{1}{3}AS^2 - \tfrac{2}{27}BS^3 + \tfrac{1}{9}CS^4. \qquad (6)$$

To find the equilibrium value of S, equation (6) is minimized with respect to S:

$$\frac{\partial f_N}{\partial S} = \tfrac{2}{3}[AS - \tfrac{1}{3}BS^2 + \tfrac{2}{3}CS^3] = 0. \qquad (7)$$

In addition to $S = 0$, which describes the isotropic phase, the solutions to this equation are

$$S_{\pm} = \frac{B}{4C} \pm \left(\frac{B^2}{16C^2} - \frac{3A}{2C}\right)^{1/2}. \qquad (8)$$

Equation (8) is an expression for the order parameter in terms of the coefficients A, B, and C. To express the order parameter as a function of temperature, we should consider the temperature dependence of these coefficients. For this purpose, we will further consider the behaviour of the system at the nematic to isotropic transition temperature, T_{NI}, at which $f_N = F_I$. Therefore,

$$AS_{NI}^2 - \tfrac{2}{9}BS_{NI}^3 + \tfrac{1}{3}CS_{NI}^4 = 0 \qquad (9)$$

where S_{NI} is the order parameter at T_{NI}. For $T = T_{NI}$, we find by combining equation (7) and equation (9), we find that when $S = S_{NI}$,

$$S_{NI}=\frac{B}{3C}. \tag{10}$$

The nematic to isotropic transition is first order [4, 18] and B must be non-zero for such a transition [4]. Therefore, C must be non-zero and have the same sign as B when S_{NI} is positive.

Using equations (9) and (10), at $T=T_{NI}$, it turns out that

$$A=\frac{B^2}{27C}. \tag{11}$$

An additional quantity, which is useful for determining the coefficients A, B, and C, is the change at T_{NI} in the entropy density, $\Delta\Sigma$. For the nematic to isotropic transition $\Delta\Sigma$ is positive and is expressed by

$$\Delta\Sigma=-\left.\frac{\partial(f_N-f_I)}{\partial T}\right|_{T=T_{NI}}=\tfrac{1}{3}S_{NI}^2\frac{\partial A}{\partial T}-\tfrac{2}{27}S_{NI}^3\frac{\partial B}{\partial T}+\tfrac{1}{9}S_{NI}^4\frac{\partial C}{\partial T}, \tag{12}$$

substituting equations (10) and (11) into equation (12), we obtain

$$\Delta\Sigma=\frac{B^2}{27C^2}\frac{\partial A}{\partial T}-\frac{2B^3}{729C^3}\frac{\partial B}{\partial T}+\frac{B^4}{729C^4}\frac{\partial C}{\partial T} \tag{13}$$

and by definition, the enthalpy of the nematic to isotropic phase transition, ΔH, is

$$\Delta H=T_{NI}\Delta\Sigma \tag{14}$$

3.2. *Temperature dependence of the coefficients A, B, and C*

We will now investigate the temperature dependences for the coefficients A, B, and C and derive expressions for the order parameter as a function of temperature and for the enthalpy of the nematic to isotropic transition. Then, we will use these temperature dependences to fit the experimental variation of the order parameter as a function of temperature to calculate the values of the coefficients.

One important criterion in our investigation of a temperature dependence for the coefficients A, B, and C was a consideration to keep the number of variable parameters to a minimum to increase their physical significance in a non-linear least squares fitting of the experimental data. Several types of temperature dependences met this criterion, but some of these types were invalid because they produced the physically meaningless result that ΔH of the nematic to isotropic transition was negative.

3.2.1. *Coefficient A*

The temperature dependence of A may be expressed by [4, 5]

$$A=a(T-T^*)^{\gamma} \tag{15}$$

where a is positive and temperature-independent, and T^* is a temperature slightly below the transition temperature, T_{NI}. γ is a constant which is considered to be unity in a mean field theory [4] such as the Maier–Saupe approach [1, 2], and this approximation has been successful for many applications [19]. We must note that in some experiments [17], γ is calculated to be a non-integer, but treating $\gamma=1$ is a more widespread approach.

This formulation for the temperature dependence of A allows its value to be small for T close to T_{NI}. Also, the free energy has a minimum for $T>T_{NI}$ and a relative maximum for $T<T_{NI}$, which is physically meaningful. The coefficient A chiefly describes the temperature dependence in the area of the isotropic to nematic transition, where the higher order terms are not as important. Because most successful applications of the Landau–de Gennes theory have concentrated in this small temperature range and have set $\gamma=1$, we assume that this condition describes well the temperature dependence in the vicinity of the isotropic to nematic phase transition. Therefore, we will use equation (15) for the temperature dependence of A with $\gamma=1$ in the three types of temperature dependence of B and C discussed below.

Based on this expression for A, equation (8) represents two solutions. For $T=T^*$, $S_-=0$ and S_+ gives $f_N<0$. Therefore, the S_+ solution represents the thermodynamically stable state, and only the expression S_+ for the order parameter will be considered.

3.2.2. *Type I temperature dependence: B and C being constants*

Let us first assume that B and C are constants with respect to temperature. Then, equation (15) may be substituted directly into equation (8) to obtain an expression for the order parameter:

$$S=\frac{B}{4C}+\left[\frac{B^2}{16C^2}-\frac{3a(T-T^*)^{\gamma}}{2C}\right]^{1/2}. \tag{16}$$

This type of temperature dependence is assumed in some applications of Landau–de Gennes theory [4, 5, 19]. The enthalpy of the nematic to isotropic transition is given by

$$\Delta H=\frac{aB^2T_{NI}}{27C^2}. \tag{17}$$

3.2.3. *Type II temperature dependence: B and C being linear with respect to temperature*

For a second type of temperature dependence, let us assume that both B and C depend on temperature linearly

$$B=b_0+b_1T \tag{18}$$

and

$$C=c_0+c_1T. \tag{19}$$

Table 1. Coefficients used in type II temperature dependence for differing values of T^*. These coefficients represent the best fit of the experimental data to equation (21) with T^* held constant during the fit. The data in this table show the fit for the carbon 2 peak of MBBA. All data for other peaks of MBBA and 5CB showed similar behaviour.

T^*/K	b_0/a_1	c_0/a_1	b_1/a_1	c_1/a_1
T_{NI}	6800	7200	− 20·8	− 21·7
T_{NI}-0·1	6800	7210	− 20·8	− 21·8
T_{NI}-0·2	6800	7220	− 20·8	− 21·7
T_{NI}-0·3	6800	7200	− 20·7	− 21·7
T_{NI}-0·4	6800	7200	− 20·8	− 21·7
T_{NI}-0·5	6800	7200	− 20·8	− 21·7
T_{NI}-0·6	6810	7200	− 20·8	− 21·7
T_{NI}-0·7	6810	7200	− 20·8	− 21·7
T_{NI}-0·8	6810	7200	− 20·8	− 21·7
T_{NI}-0·9	6810	7200	− 20·8	− 21·7
T_{NI}-1·0	6820	7200	− 20·8	− 21·7

The basis of this choice for the temperature dependence is that the temperature dependence is similar to that of A if $\gamma = 1$ (equation (15)), which may also be expressed in a linear form

$$A = a_0 + a_1 T \tag{20}$$

where $a_0 = -aT^*$ and $a_1 = a$. Notice that this choice for the temperature dependence of B and C is in accordance with a mean field type of approach to the temperature dependence of these variables.

Substituting these values into equation (8), we find there are 6 variables, a_0, a_1, b_0, b_1, c_0, and c_1, which are too many for a meaningful least squares fit of the experimental data. However, there are only 5 independent variables if the variables are expressed as ratios such as a_0/a_1, b_0/a_1, b_1/a_1, c_0/a_1, and c_1/a_1. In equation (20), $a_0/a_1 = T^*$, which may be held constant in the fitting because the fit of the experimental data is rather insensitive to the choice of T^* (see table 1) when the data are fit to the expression for the order parameter:

$$S = \frac{b_0 + b_1 T}{c_0 + c_1 T} + \left[\frac{(b_0 + b_1 2T)^2}{16(c_0 + c_1 T)^2} - \frac{3(a_0 + a_1 T)}{2(c_0 + c_1 T)}\right]^{1/2}. \tag{21}$$

Substituting these temperature dependences in equation (14), the enthalpy of the transition, ΔH, is obtained, and the form is not compact.

3.2.4. *Type III temperature dependence: B and C being non-linear with respect to temperature*

We now consider that the coefficients B and C do not have a simple linear dependence and have expressions similar to equation (15):

$$B = b(T - T^*)^{\lambda} \tag{22}$$

and

$$C = c(T - T^*)^{\eta}. \tag{23}$$

If λ and η are less than one, equations (22) and (23) would only be valid for $T_{NI} > T > T^*$, which is a very narrow temperature range. To be more general, we can rewrite equations (22) and (23) as

$$B = b(T^{\dagger} - T)^{\lambda} = B_0\left(1 - \frac{T}{T^{\dagger}}\right)^{\lambda} \tag{24}$$

and

$$C = c(T^{\dagger} - T)^{\eta} = C_0\left(1 - \frac{T}{T^{\dagger}}\right)^{\eta} \tag{25}$$

where $T^{\dagger}$ is slightly larger than T_{NI} and

$$B_0 = b(T^{\dagger})^{\lambda} \tag{26}$$

and

$$C_0 = c(T^{\dagger})^{\eta}. \tag{27}$$

Then, equation (8) becomes

$$S = \frac{b}{4c}(T^{\dagger} - T)^{\lambda - \eta} \times \left\{1 + \left[1 - \frac{24(T^{\dagger} - T_{NI})^{2\lambda - \eta}(T - T^*)}{27(T^{\dagger} - T)^{2\lambda - \eta}(T_{NI} - T^*)}\right]^{1/2}\right\} \tag{28}$$

A note should be made about this approach to the temperature dependence of B and C. If λ and η are not integers, the situation does not approximate a mean field theoretical approach to the temperature dependence. However, because mean field theory [1, 2] may not necessarily provide a proper description of the order parameter as a function of temperature, other temperature dependence of B and C must be considered as a semi-empirical approach, which hopefully will allow a description of the order parameter over the entire nematic range.

Now, let us consider a term from equation (28), $V(T)$, defined as

$$V(T) = 1 + \left[1 - \frac{24(T^{\dagger} - T_{NI})^{2\lambda - \eta}(T - T^*)}{27(T^{\dagger} - T)^{2\lambda - \eta}(T_{NI} - T^*)}\right]^{1/2}. \tag{29}$$

$V(T)$ is plotted in figure 1 for several values of $2\lambda - \eta$. Figure 1 indicates that this function is more or less constant for values of $2\lambda - \eta \geqslant 1$, deviates somewhat from constant for values of $2\lambda - \eta$ slightly less than 1, and is not constant for values far less than 1. Notice that if $\lambda = 1$ and $\eta = 1$, the temperature dependence of B and C is similar to type II temperature dependence. Thus, type III temperature is a more general case of type II temperature dependence, with the assumption noted above.

If we have the condition $2\lambda - \eta \geqslant 1$, the second term in the square bracket in equation (28) would be approximately independent of temperature, and the exact determination of λ and η is not critical. Then

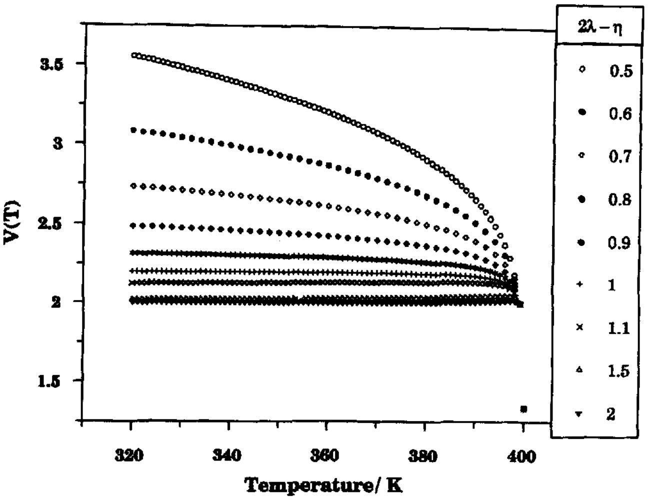

Figure 1. Equation (29) plotted as a function of temperature for several values of 2λ-η. The parameters used were $T_{\mathrm{NI}} = 400$ K, $T^{\dagger} = 400{\cdot}5$ K, and $T^* = 399$ K.

$$S \approx S_0\left(1 - \frac{T}{T^{\dagger}}\right)^f \qquad (30)$$

where $S_0 \approx b/2c$ and $f = \lambda - \eta$.

This expression is the same as the empirical Haller relation, which fits experimental data well. At $T = T_{\mathrm{NI}}$

$$S_0 = \frac{B_0}{4C_0}\left\{1 + \left[\frac{24T^{\dagger} + 3T_{\mathrm{NI}} - 27T^*}{27(T_{\mathrm{NI}} - T^*)}\right]^{1/2}\right\} \approx \frac{B_0}{2C_0}. \qquad (31)$$

Now the expression for the enthalpy of the transition is given by

$$\Delta H \approx \frac{4B_0^2}{729C_0} S_{\mathrm{NI}}^2. \qquad (32)$$

3.3. *Comparison with experimental results*

The experimental order parameters were determined through the use of a two-dimensional C-13 NMR technique which combines variable angle spinning of a liquid crystal sample with separated local field spectroscopy (SLF/VAS). We have developed this technique and have used it recently to study the orientational ordering of a large number of liquid crystals [16]. Using this method, we can obtain the order parameter at several temperatures for different molecular fragments of the molecules, such as each phenyl ring. It is practical to correlate the order parameters obtained in this manner with their C-13 chemical shifts, which are very sensitive to temperature and may be measured precisely from the one dimensional C-13 NMR spectra. We have shown that a semi-empirical relation between C-13 chemical shift and order parameter can be established [11]:

$$\Delta\delta = \alpha S + \beta \qquad (33)$$

where α and β are empirical constants, and $\Delta\delta$ is the difference between the observed and the isotropic chemical shifts of a carbon. Once the constants α and β are determined from measurements of the chemical shift and order parameters at known temperatures, the order parameters can be calculated from a chemical shift measured at any given temperature through the use of equation (33). Because the chemical shift can be determined quickly and accurately as a function of temperature in the one-dimensional spectra, it is possible to obtain a data-rich experimental curve of the order parameters for different molecular segments of the liquid crystal.

Figures 2 and 3 show the experimental variation in the

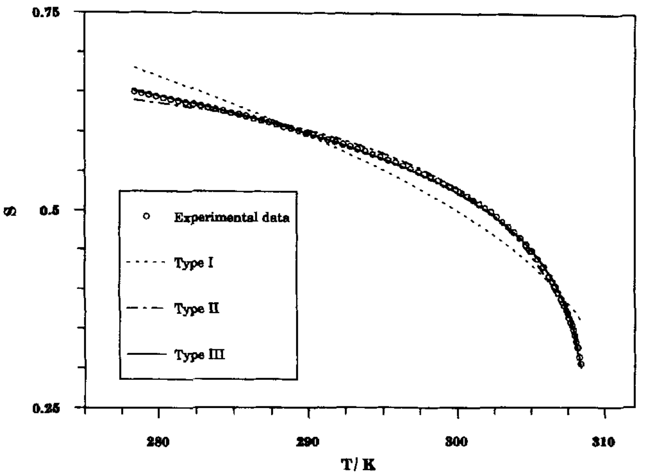

Figure 2. The variation in the order parameter of the aromatic core as a function of temperature for 5CB. The chemical shift of the 3′ carbon was used. The results for the other aromatic carbons are similar. The three types of temperature dependences discussed are fit to the experimental data.

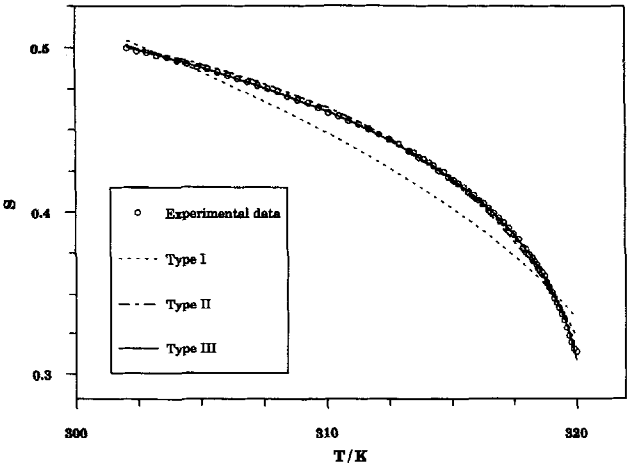

Figure 3. The variation in the order parameter of the aromatic core as a function of temperature for MBBA. The chemical shift of the 2 carbon was used. The result for the other aromatic carbons is similar. The three types of temperature dependences discussed are fit to the experimental data.

Table 2. The coefficients A, B, and C at the nematic to isotropic transition temperature, T_{NI}, for each of the three types of temperature dependences discussed in the text. Ring 1 and ring 2 represent the averaged values for two different carbons on the rings. For ring 1 of 5CB only the 3 peak was used and for ring 2 only the 3′ was used because the 2 and 2′ overlapped.

		$A/\mathrm{J\,m^{-3}}$		$B/\mathrm{J\,m^{-3}}$		$C/\mathrm{J\,m^{-3}}$	
	Type	Ring 1	Ring 2	Ring 1	Ring 2	Ring 1	Ring 2
5CB	I	$1{\cdot}74 \times 10^6$	$2{\cdot}06 \times 10^6$	$4{\cdot}90 \times 10^7$	$5{\cdot}34 \times 10^7$	$5{\cdot}12 \times 10^7$	$5{\cdot}12 \times 10^7$
	II	$2{\cdot}48 \times 10^5$	$2{\cdot}54 \times 10^5$	$1{\cdot}67 \times 10^7$	$1{\cdot}80 \times 10^7$	$2{\cdot}40 \times 10^7$	$2{\cdot}59 \times 10^7$
	III	$1{\cdot}91 \times 10^5$	$1{\cdot}85 \times 10^5$	$9{\cdot}92 \times 10^6$	$9{\cdot}41 \times 10^6$	$1{\cdot}91 \times 10^7$	$1{\cdot}77 \times 10^7$
MBBA	I	$2{\cdot}54 \times 10^6$	$2{\cdot}24 \times 10^6$	$6{\cdot}80 \times 10^7$	$6{\cdot}01 \times 10^7$	$6{\cdot}73 \times 10^7$	$5{\cdot}98 \times 10^7$
	II	$9{\cdot}36 \times 10^4$	$9{\cdot}25 \times 10^4$	$1{\cdot}56 \times 10^7$	$1{\cdot}73 \times 10^7$	$2{\cdot}35 \times 10^7$	$2{\cdot}59 \times 10^7$
	III	$2{\cdot}99 \times 10^5$	$2{\cdot}84 \times 10^5$	$1{\cdot}37 \times 10^7$	$1{\cdot}29 \times 10^7$	$2{\cdot}31 \times 10^7$	$2{\cdot}17 \times 10^7$

order parameter with temperature for 5CB and MBBA, respectively. The three types of temperature dependences were fitted to the experimental data using a non-linear least squares program. The type I temperature dependence assumes that B and C are constant and works well for 1–2 degrees below the nematic to isotropic transition temperature [4, 5, 19]. However, in the present study, the temperature dependence of the order parameters over wide nematic ranges is considered, and the fit over the entire temperature range (15–20 K) is not satisfactory (see figures 2 and 3). The poor fit may be expected, considering the increasing contribution of higher order terms in the free energy expansion at lower temperatures.

Type II temperature dependence, in which A, B, and C all depend on temperature linearly, fits the experimental data better over most of the range. In figures 2 and 3, T^* of equation (20) has been held constant at $T^* = T_{NI} - 1$, because the experimental fit is not very sensitive to the choice of T^* (see table 1). Fits for other values of T^* are similar. The improvement in the fit over type I temperature dependence implies that B and C cannot be considered to be independent of temperature. The calculated curves show some deviations from the experimental data, especially at lower temperatures, indicating that the linear temperature dependence of B and C does not accurately describe the temperature dependence of the order parameter when the higher order terms in equation (1) are neglected.

Type III temperature dependence expressed by equations (15), (24), and (25) results in excellent fits between the experimental data and the derived equations. Due to the approximations in type III temperature dependence, T^* is eliminated when equation (28) is simplified to equation (30), but the assumption in the derivation necessitates that T^* be very close to T_{NI}.

The simple relation expressed by equation (30) is the same as the Haller relation, which is a successful empirical expression for temperature dependence of the order parameter [12]. It is interesting that Haller relation and similar forms is similar to type III temperature dependent form, which is based on the Landau–de Gennes theory, provided that the temperature dependence of B and C are expressed by equations (24) and (25), respectively, with the assumption of $2\lambda - \eta \geqslant 1$. Although this assumption cannot be readily justified on a theoretical basis, the success in using equation (30) to fit the experimental data invites further exploration to study whether there is physical meaning to the variables in the fit. Below, we find several intriguing findings that suggest that there may be a link between the coefficients in equation (30) and the molecular structure.

For most liquid crystals [12], $f \approx 0{\cdot}2$, so $\lambda \approx 0{\cdot}8$ and $\eta = 0{\cdot}6$ would satisfy the condition $2\lambda - \eta \geqslant 1$. It is interesting to compare λ and η in type III temperature dependence with those in type I, for which $\lambda = \eta = 0$, and in type II, for which $\lambda = \eta = 1$, granted that the expressions for type I and type II are slightly different from type III. The exponents, λ and η, give an indication of the temperature dependence of the coefficients. Thus, it is possible to infer that type I does not allow enough temperature dependence for the coefficients, type II allows too much, while type III, which has λ and η values in between these two cases, provides a correct amount. The decreasing trend in γ, λ, and η for type III temperature dependence is an indication that the coefficients have a smaller dependence on temperature for the higher order terms in equation (6). Then, if terms with order higher than the fourth were included, they may have an even smaller temperature dependence, which may explain why it is sufficient to take the expansion to only the fourth term in equation (2) when the order parameter is not too close to unity. For order parameters close to unity, higher order terms may need to be included.

From figures 2 and 3, we see that the correct choice for the temperature dependences of A, B, and C is important to describe the experimental variation in the order parameter with temperature. Table 2 compares these coefficients at the nematic to isotropic transition tempera-

Table 3. The temperature dependent parameters of the type III temperature dependence for 5CB and MBBA for both rings of each compound given by equations (24) and (25). Ring 1 and ring 2 represent the averaged values for two different carbons on the rings. For ring 1 of 5CB only the 3 peak was used and for ring 2 only the 3′ was used because the 2 and 2′ overlapped.

	5CB		MBBA	
	Ring 1	Ring 2	Ring 1	Ring 2
B_0/J m^{-3}	$3{\cdot}00\times10^9$	$2{\cdot}80\times10^9$	$3{\cdot}12\times10^9$	$2{\cdot}98\times10^9$
C_0/J m^{-3}	$1{\cdot}52\times10^9$	$1{\cdot}38\times10^9$	$2{\cdot}11\times10^9$	$1{\cdot}96\times10^9$
λ	0·807	0·809	0·856	0·853
$f=\lambda-\eta$	0·193	0·191	0·144	0·147
$T^\dagger$/K	308·7	308·7	320·7	320·7
T_{NI}/K	308·4	308·4	320·1	320·1

ture, T_{NI}. For types I and III, the calculation of A, B, and C is possible because these parameters are also found in the relevant expression for ΔH for the different types of temperature dependence studied for type I and III (equations (17) and (32)). By equating the expression for ΔH with the experimental calorimetric data for ΔH, the values of A, B, and C at the nematic to isotropic transition were calculated and are shown in table 2. The values of ΔH used were 468 J mol^{-1} for MBBA [5] and 638 J mol^{-1} for 5CB [20]. For type II, A, B, and C can be calculated directly from equations (18–20), using the values of the experimental fit at $T^* = T_{NI} - 1$, which is approximately the T^* value observed experimentally [17]. For comparison [17], values of A, B, and C at $T = T_{NI}$ have been calculated for 8CB, which is similar to 5CB except that the aliphatic chain contains three more carbons. These values, calculated in a similar fashion to type I, are $1{\cdot}4\times10^5$ J m^{-3}, $3{\cdot}2\times10^6$ J m^{-3}, and $2{\cdot}7\times10^6$ J m^{-3}, respectively. However, these values do not provide a good fit to our experimental data of S versus temperature. These are similar to our type I results for 5CB.

Comparing the values of A, B, and C at the nematic to isotropic transition, we see that as the quality of the fits increases, the values of all three coefficients decrease, except for the type II value of A for MBBA. The ratio of C/B is about the same ($C/B \approx 1$) for types I and II but is significantly larger for type III ($C/B \approx 2$). Because the values of A, B, and C are calculated from the entire curve, we obtain an indication of the importance of the contribution of the S^2, S^3, and S^4 to the Landau expansion (equation (6)). The temperature dependence of the values of S^2, S^3, and S^4 are related to the thermal behaviour and interactions of the elements of the ordering tensor $\mathbf{Q}$ [5]. Thus, the values and temperature dependence of A, B, and C may be thought of as quantifying the importance of the various tensor elements, i.e. the structure of the liquid crystal, in determining the temperature dependence of the order parameter for that liquid crystal.

Because the liquid crystals are not rigid rods, different parts of the liquid crystal molecule involve different interactions, and it is possible to have separate and different B_0 and C_0 for each part of the liquid crystal molecule (see table 3). We note that the cause of the differences in these parameters is a difference in the order parameter of the individual rings, and we have demonstrated that different phenyl rings of liquid crystal molecules can have different order parameters depending on their substituents, which affect the rigidity of the segment [16]. It is interesting that MBBA and 5CB have approximately the same values for B_0, but C_0 is proportionally larger for MBBA. If we consider that the main core of MBBA is less rigid than the one in 5CB, then the result may imply that, for less rigid structures, the fourth order term in equation (6) is of increased importance. In equation (6), the sign of BS^3 is negative, so the free energy decreases with a larger C_0 value. This is in line with the observation between 5CB and MBBA that an increase in ΔH corresponds to a decrease in C_0. Note that in the equation for ΔH, expressed by equation (32), B_0 (see table 3) and S_{NI} (see figures 2 and 3) are approximately the same for both 5CB and MBBA whereas C_0 differs much more (see table 3).

Because the type III temperature dependence (equation (30)) is a form similar to the empirical Haller relation, it is interesting to further examine the significance of the other two parameters, S_0 and $T^\dagger$ in this relation. First, let us consider S_0. In the present derivation, $S_0 \approx b/2c$, where b and c are the temperature independent part of the coefficients of the S^3 and S^4 terms, respectively, of equation (6). Therefore, S_0 may be related to the thermal behaviour and interactions of the different ordering tensor elements.

Another parameter in equation (30), $T^\dagger$, is a temperature slightly above the nematic to isotropic transition temperature. The Landau–de Gennes theory predicts that there is a small temperature range above the nematic to isotropic transition, T_{NI}, which may be achieved by overheating the nematic sample, in which the liquid crystal phase exists but is not thermodynamically stable. In the Landau–de Gennes theory, this range is a few hundredths of a degree [4, 5]. We calculate $T^\dagger - T_{NI}$ to be about 0·3–0·6 K, so our $T^\dagger$ is most likely different from this quantity. To look more closely at what may be the physical significance of $T^\dagger$, we can consider the subject of pretransitional behaviour, in which certain observable properties deviate from their isotropic values for a few tenths of a degree above T_{NI} [17]. Well-known examples include light scattering, the Kerr effect, and magnetically induced birefringence, and explanations for the behaviour have been developed based on Landau–de Gennes theory [5, 17].

3.4. *Pretransitional behaviour*

We have observed pretransitional behaviour in liquid crystals slightly above T_{NI} through the measurement of C-13 chemical shifts, which deviate slightly from their isotropic values at higher temperatures. The effect is small, but the magnetic field used (11·7 T) provides sufficient chemical shift dispersion for the difference to be observed. As shown in figures 4 and 5, in the isotropic phase, the chemical shifts for 5CB and MBBA deviate from the asymptotic values as the temperature decreases towards T_{NI}. Of particular interest is that the deviation in the chemical shift for each type of carbon is related to their corresponding nematic chemical shift values. Thus, the CN group of 5CB shifts in a direction opposite to the aromatic peaks and the magnitude of the shift is larger because the chemical shift anisotropy of the CN is of greater magnitude and opposite sign [21]. The shifts of the aromatic carbons of 5CB and MBBA differ slightly due to the difference in the magnitude of the chemical shift anisotropy (see figures 4 and 5). Because the isotropic chemical shift of a mesogenic compound is a time average of the chemical shift tensor, the data in figures 4 and 5 suggest that incomplete isotropic averaging of the chemical shift tensor elements for the different molecular segments may be responsible for the pretransitional behaviour.

Because the observed chemical shift is related to the ordering tensor used in equation (1) [21], the pretransitional chemical shift behaviour may be related to the temperature dependence of the order parameter. Incomplete averaging of the chemical shift tensor elements implies that the ordering tensor elements are not all zero. Temperature gradients in the sample tubes for the NMR experiments prevent the determination of the transition temperature typically closer than ±0·1 K, but this precision should be sufficient for a pretransitional effect to be observed [5, 17]. In figures 4 and 5, we see that the change of the chemical shift with temperature is not linear as the clearing temperature, T_{NI}, is approached. This deviation from linearity is also seen by other methods used to investigate pretransitional effects [5, 17]. Several approaches have been used to explain the non-linear pretransitional behaviour [5, 17], many centring on local fluctuations in the isotropic phase. Usually, the explanation is complicated because of the physical nature of the technique used to measure the pretransitional behaviour. In this regard, the use of NMR chemical shifts is more direct, because of the close connection between the

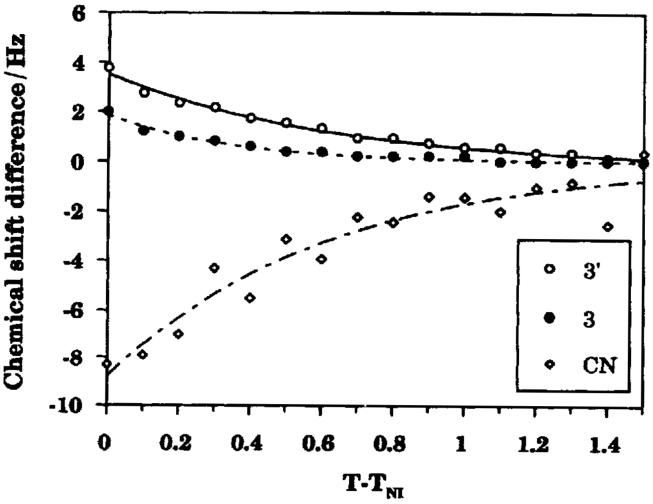

Figure 4. The variation in the chemical shift as a function of temperature above the nematic to isotropic transition temperature for several carbons of 5CB. The digital resolution was about 0·4 Hz. The lines through the data points are best fits of the data to equation (38). The CN peak frequency is assumed to have more error because its signal to noise is half of that for the aromatic peaks, which are composed of two equivalent carbon nuclei.

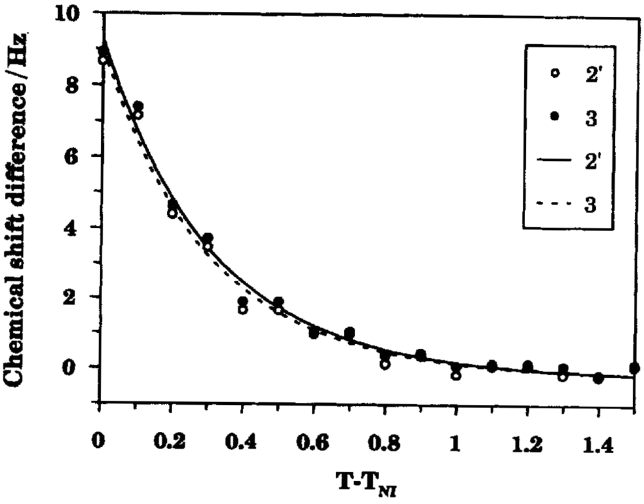

Figure 5. The variation in the chemical shift as a function of temperature above the nematic to isotropic transition temperature for two carbons of MBBA. The digital resolution was about 0·4 Hz. The lines through the data points are best fits of the data to equation (38).

observed chemical shift and the ordering tensor in equation (1).

Local fluctuations in the isotropic phase affect the free energy of the isotropic phase. In the Landau–de Gennes formalism, the contribution, $f(r)$, of the fluctuations of magnitude r to the free energy is approximated by [5]

$$\begin{aligned} f(r) = f_{\mathrm{I}} &+ \tfrac{1}{2}AQ_{\alpha\beta}(r)Q_{\gamma\delta}(r) - \tfrac{1}{3}BQ_{\alpha\beta}(r)Q_{\gamma\delta}(r)Q_{\mu\nu}(r) \\ &+ \tfrac{1}{4}CQ_{\alpha\beta}(r)Q_{\gamma\delta}(r)Q_{\mu\nu}(r)Q_{\psi\sigma}(r) \\ &+ \tfrac{1}{2}L_1[\partial_\alpha Q_{\beta\gamma}(r)][\partial_\alpha Q_{\beta\gamma}(r)] \\ &+ \tfrac{1}{2}L_2[\partial_\alpha Q_{\alpha\gamma}(r)][\partial_\alpha Q_{\beta\gamma}(r)] \end{aligned} \qquad (34)$$

where f_{I} is the free energy density of the isotropic phase without local fluctuations, $\mathbf{Q}(r)$ is the position dependent ordering tensor, and L_1 and L_2 are constants related to the conventional elastic constants. All other terms are defined as in equation (1).

Most observable properties are connected to the Fourier expansion of r. After Fourier expansion, the contribution of the fluctuations, F_{r}, for a unit volume, Ω, may be expressed by

$$F_{\mathrm{r}} = \tfrac{1}{2}\Omega A \sum_k Q^*_{\alpha\beta}(k)Q_{\alpha\beta}(k) + F_{\mathrm{E}} \qquad (35)$$

where F_{E} is the elastic contribution, $Q^*_{\alpha\beta}(k)$ is the complex conjugate of $Q_{\alpha\beta}(k)$, and the higher order terms of the ordering tensor are omitted.

According to the Landau–de Gennes theory, the probability of the appearance of a given amplitude of $\{Q_{\alpha\beta}(K)\}$ is given by a probability distribution

$$P[\{Q_{\alpha\beta}(k)\}] = \frac{1}{Z}\exp\left[-\frac{F_{\mathrm{r}}}{k_{\mathrm{B}}T}\right] \qquad (36)$$

where Z is a normalization constant, and k_{B} is the Boltzmann constant. We will now apply this formalism to the consideration of the pretransitional effect of the NMR chemical shifts.

The observed chemical shift, δ_{obs}, of a partially ordered molecular segment with C_∞ symmetry, such as the CN group of 5CB, is related to its isotropically averaged chemical shift by

$$\delta_{\mathrm{obs}} = \delta_{\mathrm{iso}} + P[\delta_{zz}]\delta_{zz} \qquad (37)$$

where δ_{zz} is the chemical shift tensor element along the zz direction defined in the molecular axis system [21]. The expressions for the chemical shifts of other molecular fragments are somewhat more complex due to their lower symmetry, and therefore these expressions for the observed chemical shifts need to include other terms from the chemical shift tensor. However, if we neglect the contributions of these terms, which are typically small, equation (37) can be regarded as an approximation for these chemical shifts. As the ordering tensor and the observed chemical shift are directly related, equations (36) and (37) may be combined. If we neglect the elastic terms in equation (35) and use equation (15) for the temperature dependence of A, the following approximation is obtained

$$\delta_{\mathrm{obs}} - \delta_{\mathrm{iso}} = \frac{\delta_{zz}}{Z}\exp\left[-\frac{(T-T^*)K_{\mathrm{f}}}{T}\right] \qquad (38)$$

where

$$K_{\mathrm{f}} = \frac{a\Omega}{2k_{\mathrm{B}}}\sum_k Q^*_{\alpha\beta}(k)Q_{\alpha\beta}(k) \qquad (39)$$

and δ_{iso} is the asymptotic value of the chemical shift in the isotropic phase. The solid curves in figures 4 and 5 show that the experimental data can be fitted very well with equation (38). Unfortunately, because the parameters K_{f} and T^* in equation (38) are tightly coupled, their values cannot be determined independently to yield the free energy of fluctuation. Nevertheless, the good fitting is encouraging and invites further theoretical and experimental exploration in the pretransitional behaviour.

4. Conclusions

We have derived several expressions for the order parameter as a function of temperature through the use of Landau–de Gennes theory and have compared these expressions to the experimental results. The second order coefficient of the Landau–de Gennes expansion is assumed to have a linear temperature dependence. It was found that the best fit was obtained from a derivation in which the third and fourth order coefficients have a non-linear temperature dependence with decreasing exponents (type III dependence). By choosing a particular temperature dependence for the coefficients in this expansion, the well-known empirical Haller equation emerges. The physical meaning of the variables in this type of temperature dependence was investigated. It was found that the tensor properties of the individual molecular fragments and the structure of the links between the fragments are important. Pretransitional behaviour was observed which can be described in terms of local fluctuations of the ordering tensor.

This type of study provides an experimental link between the molecular structure and the tensor order parameter of equation (1), which is the quantity important in the physics of the liquid crystalline phase and in the development and testing of approaches to theoretically describe and model the liquid crystal phase. We made several assumptions in our derivations for the temperature dependence of the order parameter. These assumptions seem reasonable, if we do not use a mean field theoretical approach in treating the temperature dependence of the order parameter. We must emphasize that the experimental results suggest that the assumptions we made may have some physical basis, but that they do not in themselves validate the assumptions.

The coefficients extracted did vary in a manner consistent with the molecular structure of the liquid crystals. Even if the exact physical connection between the coefficients and the structure is indirect, the ability to quantitatively determine some structure-related coefficients may prove very useful. We hope to encourage further purely theoretical descriptions in the area of the temperature dependence of the nematic order parameter to reflect the importance of molecular structure in the behaviour of the nematic phase.

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