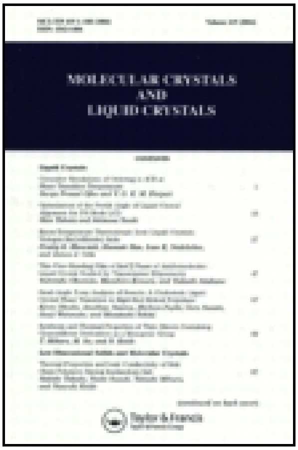

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Determination of Orientational Order Parameter in Various Liquid-Crystalline Phases

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DETERMINATION OF ORIENTATIONAL ORDER PARAMETER IN VARIOUS LIQUID-CRYSTALLINE PHASES

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Many methods for the determination of the order parameter in nematic liquid crystals are known. However, most of them are not applicable to cholesteric and smectic phases. Therefore, experimental data on the order parameter in cholesteric and smectic phases are hardly available. To determine the orientational order parameter S *we exploited the de Gennes observation, that any anisotropic physical quantity may be a measure of orientational ordering in nematic mesophase. The order parameter can be calculated directly from a macroscopic quantity measured in the experiment. From this idea we developed a simple method for the determination of the order parameter based on birefringence measurements, which can be applied for nematic, cholesteric, and smectic phases. A precise and simple method for measurement of the optical birefringence is described. An approximate empirical formula is applied for normalization of the optical birefringence similar to that used by Haller for polarizabilities. The results are in excellent agreement with the literature data. We proved that in the case of optical anisotropy the order parameter is equal within ± 1% to the one evaluated from polarizability anisotropy. Thus, the discussion concerning the local field can be omitted. Using the described method we determined the orientational order parameter in various mesophases.*

Keywords: order parameter; liquid crystal; nematic; cholesteric; smectic

INTRODUCTION

A nematic mesophase can be formed in a certain temperature range by some formanisotropic, organic molecules. Within the nematic mesophase formed by elongated molecules, a long-range orientational order of the long molecular axes is observed, without any long-range positional order of the

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molecular centers of mass. From this point of view, a nematic liquid crystal is an anisotropic, homogeneous medium with a symmetry axis parallel to the average direction of molecular long axes. A unit vector $\boldsymbol{n}$, called director, parallel to average direction of long molecular axes is attributed to each volume element of that medium. Orientational order of a nematic sample is described by the vector field $\boldsymbol{n}(\boldsymbol{r})$. Due to the orientational ordering, a nematic liquid crystal behaves like an optically uniaxial crystal and its physical properties become anisotropic. Each anisotropic quantity A, being a property of the nematic phase is no longer a scalar but rather a second rank tensor. In the coordinate system with the z-axis adjusted with direction of $\boldsymbol{n}$, this tensor has the diagonal form [3]

$$A = \begin{pmatrix} A_{\perp} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{||} \end{pmatrix} \tag{1}$$

The quantity $\delta A = A_{||} - A_{\perp}$ is called “anisotropy of physical quantity A.” For a uniaxial system, the optical anisotropy has the form $\delta \mathrm{n} = n_e - n_o$ (i.e., difference between the extraordinary and ordinary refractive indices). A quantitative description of the ordering in the case when elongated nematic molecules behave like rotatory ellipsoids or rigid rods can be done using the scalar order parameter introduced by Tsvetkov [4]:

$$S = \frac{1}{2}\langle 3\cos^2\Theta - 1\rangle \tag{2}$$

where Θ is the angle between the long molecular axis of a molecule and the optic axis. The brackets denote averaging over all directions of the long molecular axes in a small, uniformly aligned macroscopic volume. The order parameter is one of the most important material parameters of the nematic phase, which determines all of its anisotropic properties and the relations between macroscopic and microscopic properties. As this parameter is of great importance for investigations of many physical properties of liquid crystals, several methods for its determination have been developed. However, the discussion concerning the order parameter determination carried out in the literature since the 1970s is not conclusive. Nevertheless, it is widely accepted that the most exact data can be obtained from the measurements of the diamagnetic anisotropy or from the optical measurements. These methods are more precise than many spectroscopic methods and do not demand additional assumptions concerning the relative orientation of the long axis of the molecule with respect to the transition moment. The magnetic anisotropy measurements are, however, quite difficult to perform. Therefore the optical methods are used most frequently.

OPTICAL METHODS

As we already mentioned, a homogeneously aligned nematic layer behaves like a uniaxial crystal. The relationship between refractive indices and the diagonal components of the polarizability tensor of a molecule (transversal α_t and longitudinal α_l) can be obtained by modifying of appropriate equations for uniaxial crystals [5,6]. In these considerations, the main average components of the polarizability tensor are replaced by the so-called effective polarizabilities, $\alpha_{||}$ – parallel, and $\alpha_{\perp}$ – perpendicular, to the director. They are obtained by averaging molecular polarizabilities with regard to the orientation of molecules [7]. This averaging gives the following relations:

$$\alpha_{\perp} = \langle\alpha\rangle - \frac{1}{3} S \cdot \Delta\alpha,$$

and

$$\alpha_{||} = \langle\alpha\rangle + \frac{2}{3} \cdot S \cdot \Delta\alpha, \tag{3}$$

where $\langle\alpha\rangle = (2\alpha_t + \alpha_l)/3$ is the average molecular polarizability and $\Delta\alpha = \alpha_l - \alpha_t$ is the anisotropy of polarizability of the individual molecule. Chandrasekhar and Madhusudana [8] proposed a modification of the semiempirical Vuks relations originally derived for crystals [5]. In the case of nematic liquid crystals the Vuks relations take the following form:

$$\frac{n_0^2 - 1}{\langle n^2\rangle + 2} = \frac{4\pi}{3} N\alpha_{\perp}$$

and

$$\frac{n_e^2 - 1}{\langle n^2\rangle + 2} = \frac{4\pi}{3} N\alpha_{||}, \tag{4}$$

where $\langle n^2\rangle = (2n_0^2 + n_e^2)/3$ and N is the number of molecules per volume unit. These equations are known as the Vuks formulas. On the other hand, Saupe and Maier [9] introduced analogous modification of the Neugebauer [6] formula. They obtained the following relations:

$$n_o^2 - 1 = \frac{4\pi N\alpha_{\perp}}{1 - \gamma_o \alpha_{\perp} N}$$

and

$$n_e^2 - 1 = \frac{4\pi N\alpha_{||}}{1 - \gamma_e \alpha_{||} N} \tag{5}$$

where the coefficients γ_o and γ_e depend on the cavity shape and fulfill the condition $\gamma_e + 2\gamma_o = 4\pi$. To evaluate the polarizabilities one assumes that the average value of polarizability in the nematic phase is equal to its average value in the isotropic liquid. All modifications of these equations taking into account the anisotropy of molecule's shape [10] or correlation of the dipole moments of neighbor molecules [11] are in practice not very useful. The difference between the Vuks and Neugebauer models (Equations (4) and (5)) arises from the differences in the approximate description of the electric field of a light wave in the nematic medium.

To calculate the effective components of the polarizability ($\alpha_{||}$ and $\alpha_{\perp}$) using either the Vuks or Neugebauer formula the knowledge of both the ordinary and extraordinary refractive indices and the density of the nematic liquid crystal is required. The polarizabilities are connected with the main components of polarisability (α_t and α_l) and the order parameter S. To evaluate S we apply Equation (3) rewritten in the form

$$S = \frac{\delta\alpha}{\Delta\alpha} \tag{6}$$

where $\delta\alpha = \alpha_{||} - \alpha_{\perp}$ denotes the average anisotropy of the polarizability. The anisotropy of the polarizability of an individual molecule, $\Delta\alpha$, can be evaluated with the following two methods: 1) the extrapolation procedure and 2) experimental determination for the solid phase of the nematogen. The extrapolation methods are used most frequently [2,3,12]. In this extrapolation one assumes that for temperatures far enough from the clearing point, the expressions $\log(\alpha_l - \alpha_t)$ [13] or $\log(\alpha_l/\alpha_t)$ [14] are linear functions of the logarithm of the reduced temperature. On the other hand, one postulates that the order parameter is equal to 1 at absolute zero temperature (which means that all molecules are parallel to each other). Applying the extrapolation procedure one obtains $(\alpha_l - \alpha_t)$ or (α_l/α_t) from the following relations:

$$\lim_{T\to 0}(\log(\alpha_{||} - \alpha_{\perp})) = \log(\alpha_l - \alpha_t) \tag{7}$$

according to Haller [13] or

$$\lim_{T\to 0}\left(\log\left(\frac{\alpha_{||}}{\alpha_{\perp}}\right)\right) = \log\left(\frac{\alpha_l}{\alpha_t}\right) \tag{8}$$

according to Subramhanyan [14]. Actually, in most cases this is the only way to evaluate the polarizability anisotropy because the direct measurement of α_t and α_l for monocrystals of a nematogen is seldom possible. Besides, one would have to assume in this case that the molecular arrangement in the solid state is the same as in the nematic phase. In practice, this assumption is difficult to verify (in principle, it demands the X-ray studies). The estimation of the polarizability anisotropy using additivity of bond polarizabilities is very inaccurate [15].

To recapitulate, the above described typical procedure for evaluation of the long-range order parameter S using optical method follows the following scheme:

1. measurement of both refractive indexes (ordinary n_o and extraordinary n_e)
2. measurement of the density d,
3. determination of the anisotropy of the molecular polarizability $\delta\alpha$ using a local field model (Equation (4) or (5))
4. normalization procedure for the polarizability, i.e., the determination of $\Delta\alpha$ for the case of perfect order (Equation (7) or (8)), and
5. calculation of the order parameter S from Equation (6).

This procedure is quite complex and demands the determination of three physical quantities (n_o, n_e, d). In spite of this, results of order parameter determination using various local field models and using different normalization procedures differ a lot (sometimes by 10–20% [13]). Similar experimental problems occur when the S parameter is evaluated from the magnetic measurements. In this case, however, the problem of the local field does not exist.

PROPOSED METHOD FOR THE DETERMINATION OF THE ORDER PARAMETER

The anisotropy of any physical property of a nematic liquid crystal and the orientational order parameter S are mutually closely connected (see, e.g., Equation (3)). As it was pointed out by de Gennes [1], the anisotropy of any physical quantity can be a measure of orientational order. In the case of a uniaxial liquid crystal phase this parameter can be defined as:

$$Q = \frac{\delta A}{\Delta A} \tag{9}$$

where δA denotes the anisotropy of an arbitrary physical quantity A (i.e., the difference of the values A measured parallel and perpendicular to the nematic director, $\delta A = A_{||} - A_{\perp}$. ΔA stays for a hypothetical anisotropy of A in the case of the perfect order. The order parameter defined by Equation (2) may be different from that defined by Equation (9). Moreover, the values of the order parameter Q, obtained from various physical quantities, may differ from each other. Univocally defined is only the order parameter S (Equation (2)), and usually only this parameter is being determined.

Among many anisotropic physical quantities which could be used for determination of the macroscopic order parameter Q, the dielectric anisotropy for optical frequencies, $\delta\varepsilon = \mathrm{n}_e{}^2 - \mathrm{n}_o{}^2$, is especially useful. De Jeu and Bordewijk have shown that there exists good proportionality between $\delta\varepsilon$ and the magnetic anisotropy $\delta\chi$ [16]. Thus, $\delta\varepsilon$ can be used for determination of S if a local field model is applied. De Jeu [12] has also noticed that the birefringence δn can be used for this purpose as well. However, he stated that the proportionality of Δn and S is inaccurate. Probably for this reason the direct determination of the order parameter from the birefringence has never been realized.

In this paper we propose a simple procedure for the determination of the order parameter from the birefringence measurements which can be applied for nematic, cholesteric, and some smectic liquid crystal phases. According to this procedure, the scheme of order parameter determination given in chapter 2 simplifies a lot. Instead of measuring two refractive indices n_{o}, n_e and density d only the birefringence $\delta n = n_e - n_o$ is measured. The point 3 of the usual scheme is omitted. The normalization of the polarizability anisotropy $\delta\alpha$ (in the point 4) is replaced by normalization of the birefringence $\delta\mathrm{n}$. The birefringence is measured as a function of temperature and is fitted to the following form:

$$\delta n = \Delta n \cdot \left(1 - \frac{T}{T^*}\right)^{\beta} \tag{10}$$

where T is the absolute temperature, T^* and β and are constants. (T^* is about 1–4 K higher than the clearing temperature and the exponent β is close to 0.2). This procedure enables one to extrapolate δn to the absolute zero temperature. In practice, values of three adjustable parameters T^*, Δn, and β were obtained by fitting the experimental data for δn to Equation (10) written in the logarithmic form:

$$\log \delta n = \log \Delta n + \beta \cdot \log\left(\frac{T^* - T}{T^*}\right) \tag{11}$$

In our investigations, the values of $\log\Delta\mathrm{n}$ and β has been calculated by the linear regression method. The parameter T^* was adjusted to get the best correlation coefficient of the linear regression. Thus, the order parameter, according to Equation (9) is:

$$Q = \frac{\delta n}{\Delta n}. \tag{12}$$

We will demonstrate that Q determined in this way describes well the nematic order and is a good approximation of the order parameter S defined by Equation (2).

In general, the order parameter Q, defined by Equation (10), must not necessarily be identical with that defined through other tensorial properties and could be different from the order parameter S defined by Equation (2).

However, one can expect that within a given local field model, there should be a relation between Q and S. We will demonstrate it using the example of the Vuks model. From Equation (4) we have:

$$\delta n \equiv n_e - n_o = \frac{4\pi N_A d}{3M} \cdot \frac{\left(\langle n^2 \rangle + 2\right)}{n_e + n_o} \cdot \delta\alpha, \tag{13}$$

where N_A is the Avogadro number, d is density, M is molar mass of liquid crystal and $\delta\alpha = \alpha_{||} - \alpha_{\perp}$. It is widely accepted [1–3, 7–19] that $\delta\alpha$ is a measure of S (see Equation (6)). Optical anisotropy δn would be the same measure of S if the proportionality between $\delta\alpha$ and δn were fulfilled. The quantities $\langle n^2 \rangle$, n_o, n_e and density d are functions of temperature. To fulfill the condition $\delta n \sim \delta\alpha$ the parameter $d(\langle n^2 \rangle + 2)/(n_e + n_o)$ must be independent of temperature, although many parameters in Equation (13) are temperature dependent. We can account for the temperature dependence of density using the fact that the molar refraction R (defined as $R = M \cdot (\langle n^2 \rangle - 1)/d(\langle n^2 \rangle + 2) = 4\pi\alpha N_A/3$) is independent of temperature. This property of R is very well fulfilled for liquids and there is no reason to expect another behavior in the case of liquid crystals [2]. In this case d can be eliminated from Equation (13). Now Equation (13) takes the form

$$\delta n = \frac{4\pi N_A (\langle n^2 \rangle - 1)}{3R(n_e + n_0)} \delta\alpha. \tag{14}$$

The Vuks parameter V, defined as:

$$V = \frac{\langle n^2 \rangle - 1}{n_e + n_0}, \tag{15}$$

must be independent of temperature. In Equation (15) the quantities $\langle n^2 \rangle$, n_o, n_e are still temperature dependent. To check whether V in Equation (15) is constant as expected one has to apply Equation (15) for various n_o and n_e. However, these parameters may vary in relative wide ranges (approximately from 1.4 to 1.8) and are temperature dependent. For these reasons, it is useful to replace the set of parameters n_o, n_e by the set $\langle n^2 \rangle$,δn. The quantity $\langle n^2 \rangle$ is only weakly temperature dependent. On the other hand, δn is easily accessible in the experiment and its temperature dependence is similar for most liquid crystals. Hence, using relations: $\delta n = n_e - n_o$ and $\langle n^2 \rangle = (2{n_o}^2 + {n_e}^2)/3$ we can express V as function of two independent quantities δn and $\langle n^2 \rangle$:

$$V = \frac{9(\langle n^2 \rangle - 1)}{2 \cdot \sqrt{9\langle n^2 \rangle - 2(\delta n)^2} + \delta n} = const \tag{16}$$

This relation between V, $\langle n^2 \rangle$, and δn makes it possible to test the temperature dependence of the V parameter. We expect V in Equation (16)

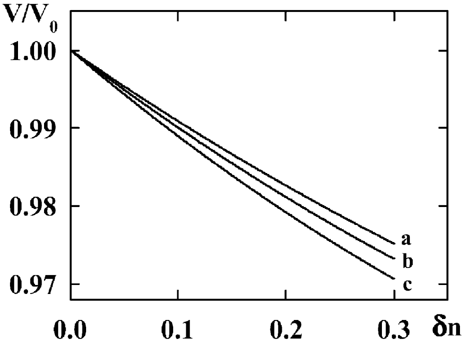


FIGURE 1 The changes of the Vuks parameter V as a function of the birefringence δn for different $\langle n^2\rangle$ values. V_0 denotes the value of V in the isotropic phase. (a) $\langle n^2\rangle = 3$, (b) $\langle n^2\rangle = 2.5$, (c) $\langle n^2\rangle = 2$.

to be only weakly temperature dependent. To check this, we apply typical values of $\langle n^2\rangle$ and δn. Usually, for nematics $\langle n^2\rangle \approx 2.5$ and δn changes from 0 to about 0.3. The quantity V calculated using these values is presented in Figure 1. It is obvious from this figure that Vuks parameter V changes less then ±1.5% for experimentally observed values of δn and $\langle n^2\rangle(\delta n \in (0{,}0.3)$ and $\langle n^2\rangle \in (2{,}3))$.

In practice, $\langle n^2\rangle$ slightly decreases with temperature. This leads to the compensation of the weak temperature effect of $\langle \mathrm{n}^2\rangle$ and suppresses the temperature changes of V well bellow ±1%. Hence, as the above discussion demonstrates, we can assume $V = Const(T)$ with good accuracy and thus $\delta n \sim \delta\alpha$ in the case of the isotropic Vuks' local field.

In principle, similar considerations ought to be performed for the anisotropic local field, e.g., in the framework of the Neugebauer [6] model. In this case, however, two additional parameters γ_e and γ_o appear, and one of them is arbitrary. Unfortunately, no method for independent determination of this parameter is known. Hence, it is not possible to find an unambiguous relation between δn and $\delta\alpha$ (like Equation (14)) in the case of an anisotropic local field.

EXPERIMENTAL

The measurement of the optical birefringence is much easier than the measurement of both refractive indices. Interference methods are often used for this purpose [20,21]. One of the most frequently used methods is the wedge method [21]. In this method distances between interference fringes in a wedge-shaped sample are measured. Apart from many advantages of this method, it has one drawback: difficulties in precise determination of the wedge angle. This angle can change during the experiment (e.g., after filling the measuring cell or after crystallization of the sample). Further, the wedge angle undergoes irreversible changes as a function of time and temperature. For these reasons we made a modification of the wedge method. In our experiment the measuring cell of variable thickness consisted of a plane glass plate and a plane-convex lens of known curvature radius (Figure 2a). The radius of curvature of the lens can be determined with the great accuracy (e.g., using the Newton rings method). The R value is very stable and does not change with temperature. The lens was already used for the refractometric measurements by Chatelain as early as 1937 [22]. There is, however, an important difference between our and Chatelain's experiment. Chatelain observed the interference rings resulting from interference of light rays reflected on the surface of plate and lens. In this way he measured both refractive indices separately. In our experiment, the glass plate and lens are placed between the crossed polarizers on a microscope stage. After introducing a liquid crystal into the gap between lens and plate, a system of concentric rings can be observed (Figure 2b). These rings result from interference of the ordinary and extraordinary rays after passing the analyzer. Thanks to the crossed polarizers arrangement and interference of transmitted rather than reflected rays the rings are very distinct, even if the alignment of the sample is not perfect.

The optical path difference of the ordinary and extraordinary waves $y \cdot \delta n$ corresponding to a given bright ring is $k \cdot \lambda$ (y denotes the sample thickness in the middle of the ring, λ is the wavelength of light, and k is order of interference, i.e., the successive ring number). The thickness y can be calculated from the form

$$y = \frac{x^2}{2R}, \tag{17}$$

where x denotes the radius of the considered ring (Figure 2a). Thus, the birefringence δn can be determined with a great accuracy (better than 10^{-3}) from the slope of the straight line representing the x^2 on k dependence (Figure 3). The same result can be obtained when the dark rings are considered.

RESULTS AND DISCUSSION

To check the proposed method we have performed measurements on the well-known nematic liquid crystal, paraazoxyanizole (PAA). We choose this material because there exists a lot of literature data on the temperature dependence of the order parameter in this substance. The order parameter

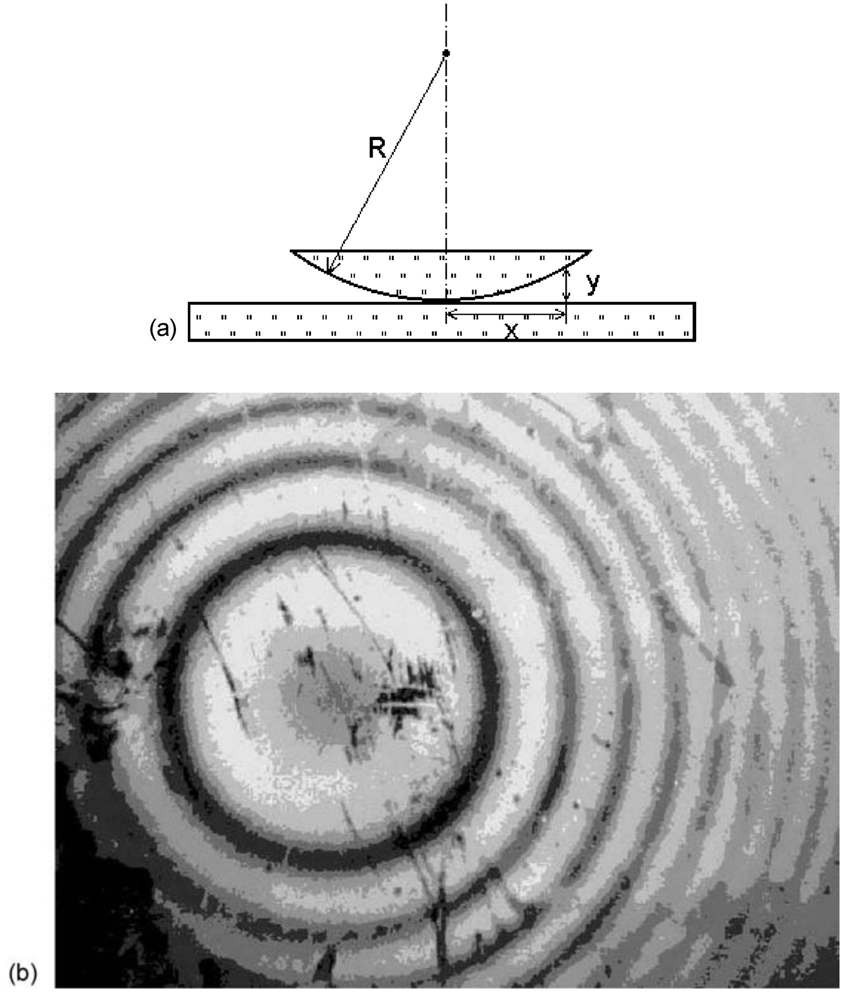


FIGURE 2 (a) The geometry of the measuring cell used for the birefringence determination. (b) The interference pattern of the nematic PAA at temperature 137.5°C (lens curvature radius $R = 13.5\,\mathrm{mm}$, wavelength $\lambda = 546\,\mathrm{nm}$, magnification 90×).

S of PAA has been measured by many authors using various methods. We measured temperature dependence of the birefringence. To determine S we used the value of $\Delta n = 0.403$ in Equation (6), which was determined with the extrapolation procedure described above (Equation (11)). The extrapolation procedure applied for δn does work very well, not worse than the original Haller procedure [18] applied for the product of the molecular

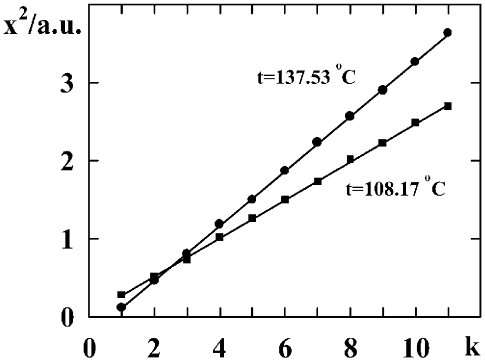


FIGURE 3 Squares of radii of successive interference rings, plotted as function of the ring number *k*, measured in PAA at different temperatures.

polarizability and the order parameter. The validity of δn extrapolation is additionally confirmed by results of δn measurements performed in the solid state (see Figures 2b and 4) which appeared to be the same as the extrapolated value.

The extrapolated value $\Delta n_{extr} = 0.403$ is, within experimental accuracy, the same as δn value measured in the solid state, $\Delta n_{crys} = 0.403$. Such an agreement is not always present (it depends on the crystal structure). The value of Δn_{crys} must never exceed Δn_{extr} if the extrapolation procedure is correct. In all cases when we have managed to measure Δn_{crys} the relation $\Delta n_{extr} \geq \Delta n_{crys}$ was fulfilled.

Some of the literature data concerning the temperature dependence of the order parameter of PAA measured with various methods are reviewed in Figure 5. It can be seen from this figure that the values of S obtained with various methods differ quite strongly (up to ± 20%). Our results obtained using the method described in Chapter 3 match in the middle of results from other methods usually considered to be exact. We obtained similar results for other nematic liquid crystals, e.g., n-pentyloxy-cyanobiphenyl (5OCB) or n-octylcyanobiphenyl (8CB).

The orientational order has often been studied in nematic liquid crystals but rarely in smectic and cholesteric liquid crystals. The cholesteric liquid crystals are spontaneously twisted nematics. We therefore expect to be able to characterize the average orientation of molecules in a cholesteric liquid crystal with the same set of order parameters as in nematics, with the distinction that the cholesteric order is defined relative to a local coordinate system twisting along the optic axis. From this point of view, there is no distinction between nematics and cholesterics—locally they have the same symmetry. The birefringence measurement, described before, can be

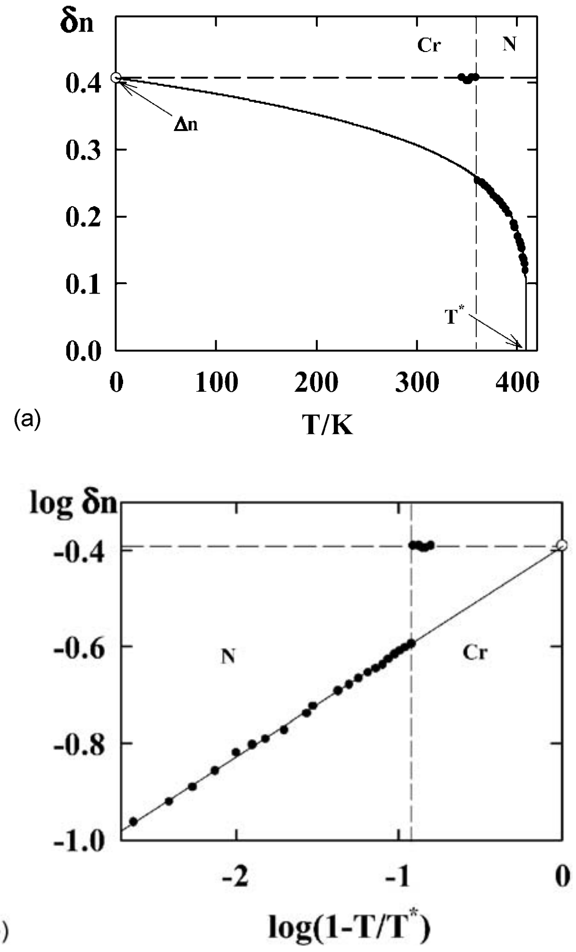


FIGURE 4 (a) Temperature dependence of the birefringence δn for PAA in the nematic (N) and crystalline (Cr) phases measured by the proposed "lens" method. The solid line shows the fitting of δn (in the nematic phase) to Equation (10) and extrapolation (open circle) to the absolute zero temperature. (b) The extrapolation of the birefringence δn of PAA to the temperature of the absolute zero (using Equation (11)). The extrapolated value $\Delta n_{extr} = 0.403$ is, within the experimental accuracy, the same as Δn value measured in the solid state, $\Delta n_{crys} = 0.403$.

used to determine the order parameter for cholesteric liquid crystals, too. However, in this case there is a small difference in the experimental procedure as compared with nematics. In the nematic phase we observed interference rings in a planar cell (the director parallel to glass plates). In the case of cholesterics the helix axis must be parallel to the glass plates.

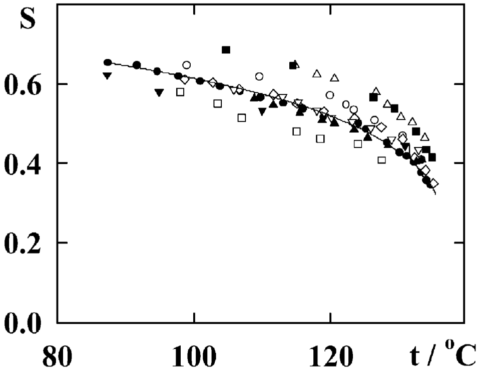


FIGURE 5 The review of data on temperature dependence of the S parameter for PAA. The results were obtained using various methods: ○ and ◇, from diamagnetic anisotropy [7,23]; ▽, from refractometry using the Vuks model [30]; ▼, from absorption of UV polarized light [30]; □, from IR absorption [9]; ■, from refractometry and NMR [17]; △, from refractometry using the Lorentz tensor [15]; ▲, from refractometry using the Neugebauer model [9]. Full circles (●) and solid line present our results.

We observed interference rings caused by the birefringence only for "finger print" or "focal conic" texture. When we used well-oriented planar sample in the Grandjean texture (the helical axis perpendicular to the glass plate) we observed dark and bright rings caused by the optical activity and not by the birefringence.

In the literature, only data on cholesteryl nonanoate are available [24–28]. Therefore, in order to test our method we carried out measurement for the same compound. This cholesterol derivative has the cholesteric and smectic A phases. Figure 6 presents results of our birefringence measurement performed as a function of temperature.

We determined the orientational order parameter using the method described in section 3 using δn data measured in the cholesteric phase. The extrapolated value $\Delta n_{extr} = 0.0713$ is nearly the same as the Δn value measured in the solid state ($\Delta n = 0.0711$). The extrapolated value of the birefringence was used to determine the S parameter in both the cholesteric and the smectic A phase (Figure 7). We obtained very good agreement with the literature data in both mesophases [24–28].

It is obvious from Figure 6 that the changes of the birefringence in the entire range of the smectic A phase are small. Therefore the extrapolation procedure applied for the birefringence data obtained in the smectic A phase gives inaccurate values of all three adjustable parameters (Δn, T^*, and β in Equation (11)). Hence, our procedure is safe only when

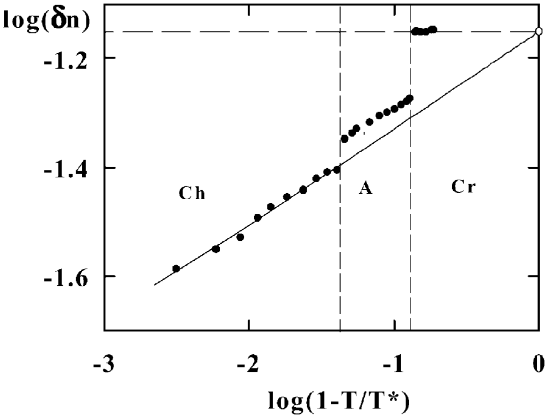


FIGURE 6 The log–log plot of the birefringence δn versus reduced temperature for cholesteryl nonanoate in the cholesteric (Ch), smectic A (A), and crystal (Cr) phases measured using the method described in this paper. The solid line illustrates the extrapolation of δn to the temperature of the absolute zero (open circle).

the investigated material has sufficiently wide temperature range of the nematic phase.

Figure 8 presents the interference pattern of 8-OCB in the nematic phase (Figure 8a) and in the solid state (Figure 8b). The temperature dependence of δn for the nematic, smectic A and crystalline phases measured by the described method is shown in Figure 8c. The extrapolated value $\Delta n = 0.232$ is almost the same as Δn measured in the crystalline state ($\Delta n = 0.231$). We used this value to determine the S parameter in both liquid-crystalline phases.

Figure 9 presents the comparison of our measurement for 5CB (solid line and black points) with literature data [29] obtained from the polarizability anisotropy using the Vuks local field model. The agreement of results obtained in the nematic phase is very good.

The proposed method can be applied for other smectic phases as well. As an example we show in Figure 10 the results obtained for di-heptyloxyazoxybenzene (HOAB) in their nematic and tilted smectic C phases.

CONCLUSIONS

A simple and very precise method for determination of the optical birefringence as function of temperature is described in this work. In the proposed method we made a modification of the wedge method [2] by using

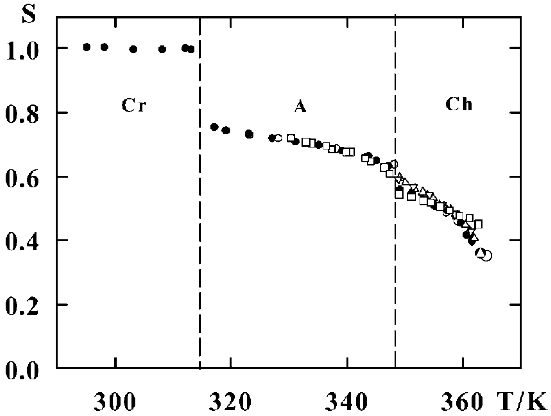
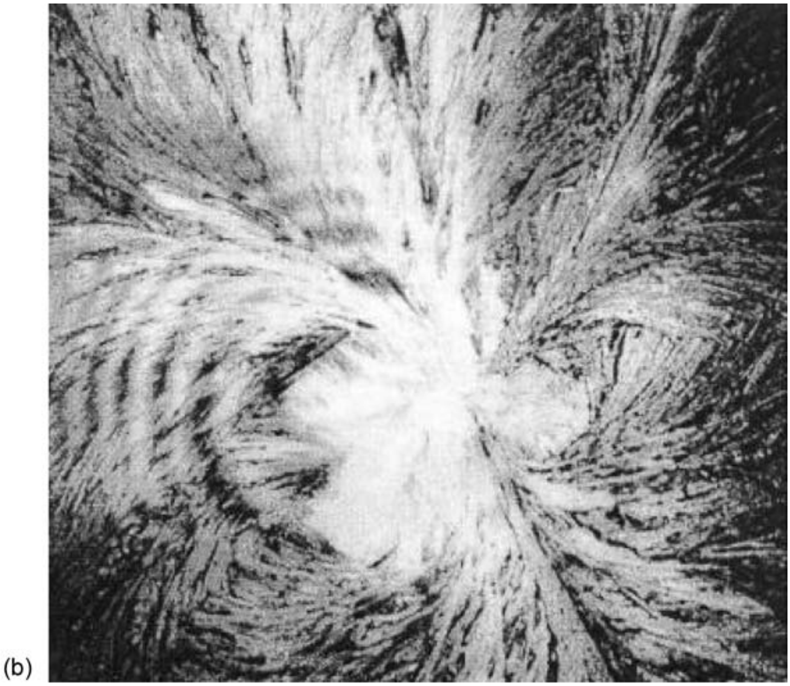


FIGURE 7 The temperature dependence of the order parameter of cholesteryl nonanoate determined using the proposed method (black points) and using the Vuks local field model for the polarizability anisotropy: squares, from Adamski and Dylik-Gromiec [24]; down triangles, from Avierianov and Shabasov [25]; up triangles and circles, using NMR [26–28].

FIGURE 8 The interference pattern of 8-OCB (wavelength $\lambda = 546\,\text{nm}$, magnification 90×): (a) in the nematic phase at 77°C; (b) in the solid state at 35°C, (c) the temperature dependence of the birefringence δn for 8-OCB in the nematic, smectic A, and crystal phases measured using the proposed method. The solid line presents the fitting of δn to Equation (11) in the nematic phase.



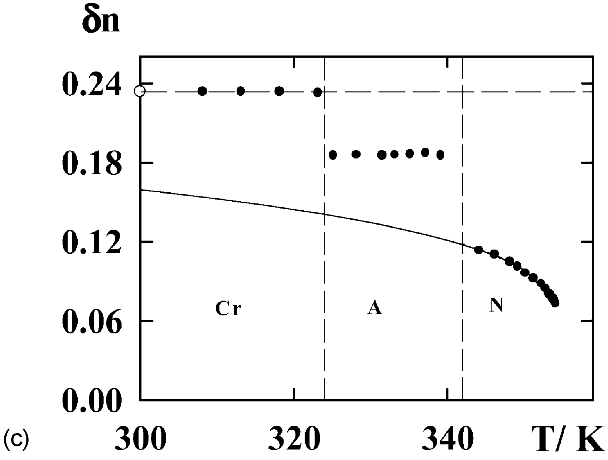


FIGURE 8 (Continued).

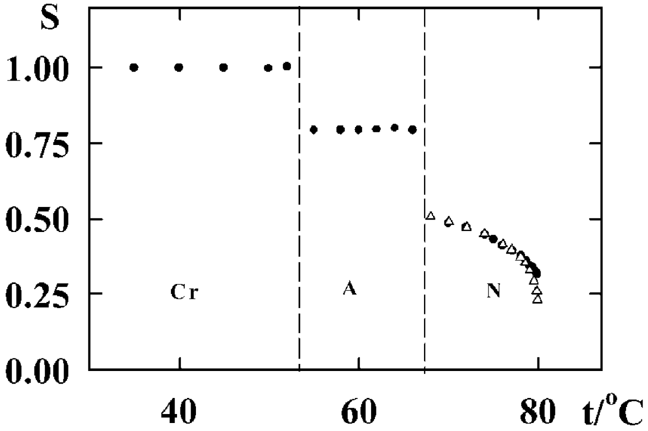


FIGURE 9 The temperature dependence of the S parameter for 8-OCB determined using the described method (full circles) and using the Vuks local field model for the polarisability anisotropy (triangles, after Mitra [29]).

the lens. We can use this "lens" method for δn determination in nematic, cholesteric, and smectic liquid crystal phases. Sometimes we were able to perform measurement in the crystalline phase as well. The birefringence δn can be measured with great accuracy (better then $\pm 10^{-3}$ in all liquid-crystalline phases). We elaborate a simple method for the determination of the orientational order parameter in liquid crystals based solely on the birefringence measurements. We exploited the de Gennes observation that any macroscopic physical quantity may be a measure of orientational order in the nematic phase. We proved that the order parameter could be calculated directly from the macroscopic quantity—the birefringence, in a similar way as in the case of the Haller method applied for the polarizability. The value of the birefringence Δn for a hypothetical, ideally ordered nematic could be extrapolated from the temperature dependence of δn. This value can be also used for the determination of the order parameter in cholesteric and smectic liquid crystals. The extrapolation procedure for $\delta n(T)$ proposed in this work does not undergo restrictions resulting from the choice of the local field model, because we applied the extrapolation not for the polarizability anisotropy (where we must have used a local field model) but directly for the birefringence. The birefringence δn has been very precisely measured as a function of temperature in nematic, smectic, cholesteric, and sometimes even in the crystalline phase. When we know the birefringence for crystalline state Δn (where orientational order is equal to 1—as it would be in a perfectly ordered nematic liquid crystal) we can determine S from the ratio $\delta n(T)/\Delta n$. Alternatively we can determine

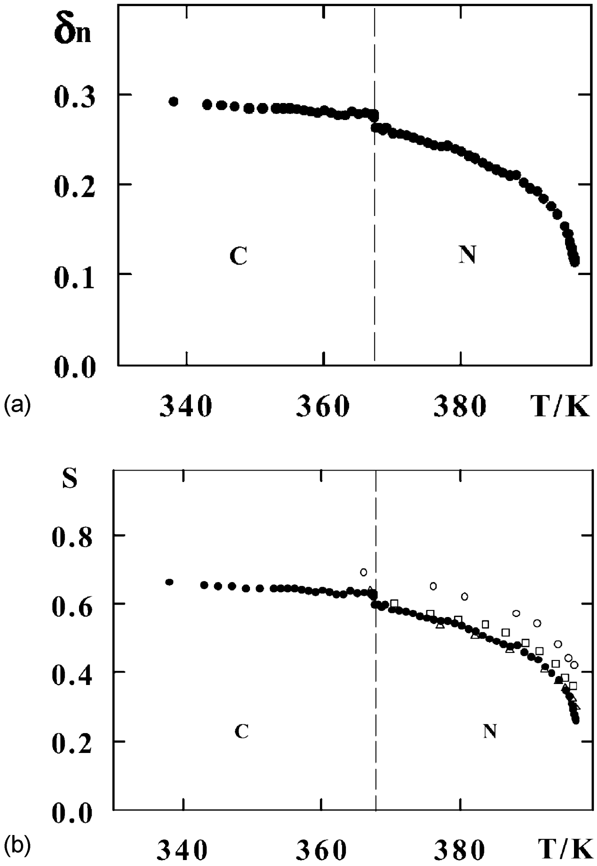


FIGURE 10 The temperature dependence of the birefringence (a) and the S parameter (b) in the anisotropic phases of HOAB obtained by the described method (full circles) and its comparison with the literature data for the nematic phase (circles, from Hansan and Shen [17]; squares, from de Jeu and Bordevijk [16]; triangles, from de Jeu and Claassen [23]).

Δn using an extrapolation procedure. We fitted $\delta n(T)$ to Equation (11) using three adjustable parameters Δn, T^*, and β. These three parameters can be easily obtained by fitting the experimental data to Equation (11) written in the logarithmic form. In this case the values of Δn and β were calculated by the linear regression method, treating T^* as the primary adjustable parameter. The Δn value obtained using this procedure was in excellent agreement with Δn measured in the crystalline phase. This result suggests that the anisotropy of the local field in both the nematic and the crystalline phase is negligible. The S results obtained for PAA, 8-OCB, and cholesteryl nonanoate are in very good agreement with the literature data obtained using different methods (see Figures 5, 7, and 9), mostly from the anisotropy of either magnetic susceptibility or electric polarizability. We have presented a general argument that the order parameter determined directly from the birefringence is consistent with S calculated from the polarizability. As the used method of determination of orientational order parameter is very simple, has the theoretical background and gives good results, we think it can be useful in both laboratory practice and teaching.

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