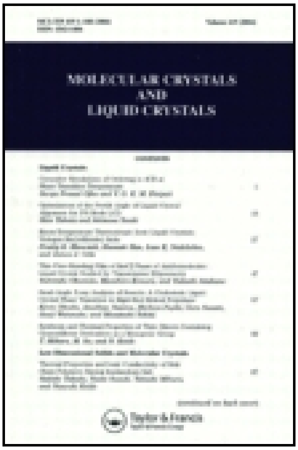

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Influence of the Orientational Order on the Optical Properties of Cholesteric Liquid Crystals

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Influence of the Orientational Order on the Optical Properties of Cholesteric Liquid Crystals

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An orientational order parameter for cholesteric liquid crystals is defined in analogy to nematic mesophases. The influence of this parameter on the selective reflexion and the optical rotatory dispersion is described. Its relative change with temperature is evaluated from ORD measurements for an induced cholesteric solution and is found to be similar to that known for nematic liquid crystals.

I INTRODUCTION

The essential feature of nematic liquid crystals is the parallel ordering of the molecular long axes. A parameter describing the order quantitatively was defined by Maier and Saupe[1] and different methods are known to determine it experimentally.[2] With the increase of interest in cholesteric liquid crystals a demand for a comparable quantity for this type of mesophases has been growing. An experimental attempt using NMR spectroscopy was reported very recently.[3] In order to obtain well defined signals fluorine NMR had to be applied, a fact which restricts the applicability. In this paper the influence of an ordering parameter on some optical properties of cholesteric liquid crystals is examined.

Starting from the dependence of the refractive index on the ordering parameter as pointed out by Saupe and Maier[2] for nematic mesophases, and using the formulae for the selective reflexion and the optical rotatory dispersion derived by Chandrasekhar *et al.*[4] one arrives at simple relations between the results from such measurements and the ordering parameter. As these phenomena are inherent properties of the cholesteric state the determination is possible for all cholesteric samples independent of type and constitution of the molecules.

II ORDERING PARAMETER

The ideal nematic mesophase consists of molecules ordered parallelly, the direction of the long axes thus defining the director of the structure. In a real nematic liquid crystal the long axis of an individual molecule forms an angle θ with the director. Averaging leads to the ordering parameter S[1]

$$S = (2 - 3\sin^2\theta)/2 \tag{1}$$

This quantity can be experimentally determined,[2] e.g. from the refractive index, the linear dichroism or the NMR spectrum of the nematic sample.

A cholesteric liquid crystal is closely related to nematic mesophases, it can be regarded as being a twisted pile of two-dimensional nematic layers. The axis of this pile—perpendicular to the layers and perpendicular to the long axes of the molecules—constitute the optical axis. On proceeding along it the orientation of the molecules and hence the director rotate uniformly. This helical structure can be characterized by its pitch and its handedness.

The striking property of a cholesteric liquid crystal is the selective reflexion of circularly polarized light whose wavelength equals the pitch and whose direction of polarization matches the handedness of the structure. In such a case the director (describing the orientation of the molecules) and the electric vector (describing the momentary direction of polarization) rotate synchronously. Therefore, the angle between the local director and the acting electric vector is the same everywhere. From this point of view, it is an analogy to treating a nematic liquid crystal with linearly polarized light. Due to this, we may use Eq. (1) as the definition of an orientational order parameter for the cholesteric mesophase, θ here being the angle between the molecular long axis and the *local* director. For this wavelength λ_R

$$\lambda_R = \lambda/n = p \tag{2}$$

(λ wavelength in vacuo, n mean refractive index, p pitch) which is selectively reflected the optical properties of a cholesteric sample are expected to depend on S in the same way as those of a nematic sample do. Starting from this analogy, the dependence of the refractive index of nematic layers on the ordering parameter can be used to express the influence of S on the reflexion of a cholesteric pile.

III REFLEXION BY A CHOLESTERIC PILE

The selective reflexion $R(\lambda)$ and the corresponding optical rotatory dispersion $\Phi(\lambda)$ had been calculated by Chandrasekhar *et al.*[4] on the basis of the pile model for the cholesteric helical structure. Due to the angle between the orientations of two adjacent layers at each "boundary" the incident light is partly reflected. The superimposed reflexion of all layers belonging to one period (equal to the pitch) is described by the reflexion coefficient Q_0[3]

$$Q_0 = 2\pi(n_1 - n_2)/(n_1 + n_2) \tag{3}$$

n_1 and n_2 being the main values of the refractive index of one pseudo-nematic layer. For nematic liquid crystals the dependence of the refractive indices on the ordering parameter was derived by Saupe and Maier[2] using the Lorentz–Lorenz equation to express the indices in terms of the polarizability ($\bar{\alpha}$ mean value; α_l, α_q main values). Defining

$$\beta = \tfrac{4}{3}\pi N\bar{\alpha} \tag{4}$$

(N the number of molecules per cm^3) and

$$s = \tfrac{4}{9}\pi N(\alpha_l - \alpha_q)S \tag{5}$$

we rewrite their results

$$n_1^2 = \frac{1 + 2(1 + a)(\beta + 2s)}{1 - (1 - 2a)(\beta + 2s)} \equiv \frac{h^2}{k^2} \tag{6a}$$

$$n_2^2 = \frac{1 + (2 - a)(\beta - s)}{1 - (1 + a)(\beta - s)} \equiv \frac{l^2}{m^2} \tag{6b}$$

where the parameter a accounts for the internal field correction.

The refractive indices in Eq. (3) can be identified by those for a nematic mesophase given by Eqs. (6) because of the (pseudo-)nematic character of the layers the considered cholesteric mesophase consists of. We find

$$Q_0 = 18\pi[s + a(\beta^2 + \beta s + 2s^2)]/f(S) \tag{7}$$

where

$$f(S) = (hm + kl)^2 \tag{7a}$$

If the internal field correction is neglected ($a = 0$) the second term of the numerator of Eq. (7) vanishes and the reflexion coefficient becomes

$$Q_0 = 8\pi^2 N(\alpha_l - \alpha_q)S/f(S) \tag{8}$$

Using data from the literature[2] β becomes roughly 0.3 and s decreases from about 0.08 to 0.04 on decreasing S. Within this interval $f(S)$ decreases monotonously from 4.461 to 4.433, this change is about 0.6%. For $\beta = 0.5$ a decrease of about 2.7% and for $\beta = 0.1$ an increase of about 0.8% is calculated. We, therefore, may use the approximation that the reflexion coefficient Q_0 is proportional to the ordering parameter

$$Q_0 = Q_1 S \tag{9}$$

Applying the internal field correction means an increment to the numerator of Eq. (7). The increment, however, is small compared with s and its influence on Q_0 is partly balanced by the likewise increased denominator. For the quoted parameters the proportionality (Eq. 9) is also fulfilled within the order of 1 to 2%.

IV SELECTIVE REFLEXION

An equation describing the selective reflexion R of a cholesteric sample as a function of the wavelength was derived by Chandrasekhar *et al.*[4] Converting the equation from wavelengths to wavenumbers $\tilde{\nu} \equiv 1/\lambda$ ($\tilde{\nu}_R$ center of the selective reflexion) and using a slightly different notation, it is rewritten

$$R(\tilde{\nu}) = Q^2/(\varepsilon^2 + \xi^2 \coth^2 m\xi) \tag{10}$$

where

$$\varepsilon = 2\pi(1 - \tilde{\nu}/\tilde{\nu}_R) \tag{10a}$$

$$Q^2 = Q_0^2(\sin^2 \varepsilon)/\varepsilon^2 \tag{10b}$$

$$\xi \simeq (Q^2 - \varepsilon^2)^{1/2} \tag{10c}$$

A sample of thickness d consists of m periods, hence

$$m = d/p = dn\tilde{\nu}_R \tag{11}$$

Due to the above shown dependence of Q_0 on S the reflexion is a function of the ordering parameter. At the center of the reflexion band ν equals ν_R and here are $\varepsilon = 0$ and $\xi = Q$. For maximum reflexion at ν_R, therefore, Eqs. (10) reduce to

$$R_R = th^2 mQ \tag{12}$$

Using Eqs. 9 and 11 and

$$\lim_{\varepsilon \to 0} \frac{\sin^2 \varepsilon}{\varepsilon^2} = 1 \tag{13}$$

Eq. (12) can be rewritten as

$$R_R = th^2(dn\tilde{\nu}_R Q_1 S) \tag{14}$$

if the proportionality Eq. (9) is assumed to be valid.

V OPTICAL ROTATORY DISPERSION

The rotatory dispersion of a cholesteric sample in a spectral region free of absorption is given by[4]

$$\Phi = \left\{\varepsilon - \frac{1}{m}\operatorname{arctg}\left(\frac{\varepsilon}{\zeta}\operatorname{tg} m\zeta\right)\right\} \Big/ 2p - \frac{\pi}{4}(n_1 - n_2)^2 p\tilde{\nu}^2 \tag{15}$$

where

$$\zeta = (\varepsilon^2 - Q^2)^{1/2} \tag{15a}$$

The second term gives a monotonous background rotation while the first term describes a rotatory anomaly around $\tilde{\nu}_R$ of a shape similar to a Cotton effect. A graph of this function in the vicinity of $\tilde{\nu}_R$ is shown in Figure 1. Due to the dependence of Q on S the rotation is influenced by the ordering parameter.

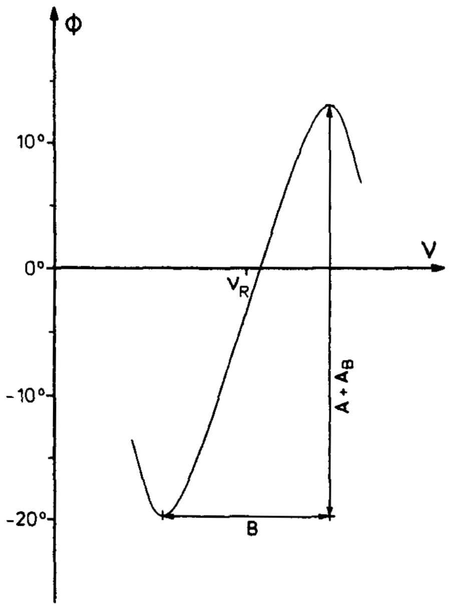

FIGURE 1 Optical rotation in the vicinity of the selective reflection band as calculated from Eq. (15) using $\tilde{\nu}_R = 2000\ \mathrm{cm}^{-1}$, sample thickness $d = 26\ \mu\mathrm{m}$, mean refractive index $n = 1.7$, $Q_0 = 0.3$.

Confining ourselves to the first term of Eq. (15) we find extreme values for

$$\pm m\zeta = \pi/2 \tag{16}$$

The difference between the so defined wavenumber $\tilde{\nu}_1$ and $\tilde{\nu}_2$ for maximum and minimum rotation, respectively, is the width B of the anomaly (compare Figure 1)

$$B = (1 + r^2S^2)^{1/2}/2nd \tag{17}$$

where

$$r = \frac{2}{\pi} nd\tilde{\nu}_R Q_1 \frac{\sin\varepsilon}{\varepsilon} \tag{17a}$$

The amplitude A defined as the difference between maximum and minimum rotations (compare Figure 1) becomes

$$A = \{(1 + r^2S^2)^{1/2} - 1\}\pi/2 \tag{18}$$

with the understanding that Q_0 is proportional to S (Eq. 9).

The contribution of the monotonous background rotation as given by the second term of Eq. (15) can be taken into account by interpolating from the rotatory curve well outside the anomaly or otherwise by the following calculation. For the contribution of the background rotation at the peaks of the rotatory anomaly (wavenumbers $\tilde{\nu}_1$, $\tilde{\nu}_2$) we have from Eq. (15)

$$\rho_{1,2} = \pi nd\left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 \frac{\tilde{\nu}_{1,2}^2}{\tilde{\nu}_R} \tag{19}$$

$(n = (n_1 + n_2)/2)$. It can be shown that the difference $\rho(\tilde{\nu}_1) - \rho(\tilde{\nu}_2) \equiv A_B$ is given by

$$A_B = ndBQ_0^2/2\pi \tag{20}$$

Eq. (18) can be rewritten by using Eq. (17)

$$A = (2ndB - 1)\pi/2 \tag{21}$$

An experimentally determined amplitude equals the sum of the contributions A and A_B owing to the first (rotatory anomaly) and second term (background rotation), respectively, which can be separated by applying Eqs. (20) and (21) using the measured width B.

The expressions for the amplitude A and the width B contain the factor $\sin\varepsilon/\varepsilon$ which—as stated above—may be neglected for small values of ε. If a correction is necessary this can be done using the measured width because due to the definition of B we may substitute

$$\varepsilon_{1,2} = \pm\pi B/\tilde{\nu}_R \tag{22}$$

Q_1 depends on the wavelength due to being a function of the refractive indices. These, however, will not change significantly within the wavenumber interval between maximum and minimum rotation of the rotatory anomaly when it is observed within a spectral region free of absorption.

VI DISCUSSION

Due to the fact that the reflexion coefficient can be expressed in terms of the orientational order parameter S the selective reflexion and the amplitude of the rotatory anomaly depend on S. This in turn allows to evaluate S from the experimental results. Provided that the molecular polarizabilities are known, the absolute value of S can be calculated. Even without this knowledge, Eqs. (14) and (18) allow to determine the relative change of S upon changing experimental parameters such as temperature, pressure, composition of cholesteric mixtures, concentration of chiral guest molecules in nematic liquid crystals ("induced cholesteric solutions"), contaminations etc. For nematic liquid crystals the temperature dependence of the ordering parameter has turned out to be of special importance, a similar tendency can be expected for cholesteric mesophases.

Out of the methods described here for the determination of the ordering parameter S the measurement of the reflexion is the more direct approach as far as neglections or corrections are concerned. Due to the hyperbolic tangent in Eq. (14) the results can be optimized by adjusting the sample thickness. If for instance the temperature dependence of S is studied from its highest value at the melting point down to about half this value at the clearing point the largest change in reflexion is caused if (for highest S values) $mQ_0 \approx 1.5$. Results obtained in the visible part of the spectrum can be fitted[4] with $Q_0 = 0.1$. Therefore, the sample should consist of about 15 periods, i.e. about 5 μm. For experiments in the infrared spectral region Q_0 seems to be larger by a factor 3. Due to the larger wavelength, however, a thicker sample is required.

Some difficulties arise from the fact that the reflection normally has to be studied under angles of incidence and reflexion different from zero. As a consequence the reflexion band is shifted and lowered. Fergason gave a formula[5] to correct the wavenumber on the basis of the Bragg equation and Snellius' law; the amplitude can be corrected by the theory of multi-layer interference. This becomes all the more necessary the more the angle of incidence increases. The evaluation will be further complicated if an integration is required due to the aperture angle. Finally, the reflexion at the surface of the cell windows has to be taken into account.

Contrary to the reflexion the measurement of the optical rotation is less complicated by experimental obstacles. Usually the aperture angle is small and around zero thus causing less distortion. The measurement depends on the intensity only in so far as the signal-to-noise ratio is concerned. The selective reflexion lowers the transmitted intensity by 50% only around $\tilde{\nu}_R$ providing higher intensities at the minimum and the maximum of the rotatory anomaly. Another advantage is the free choice of the sample thickness, so that the operational range of the polarimeter can be fully used. From this point of view the rotatory dispersion is the more appropriate method to study the orientational order parameter for cholesteric samples.

VII EXAMPLE

The temperature dependence of an induced cholesteric solution shall serve as a first example. We have been interested in such solutions because their selective reflexion and even more the optical rotatory dispersion offer new methods to study the chirality of the solute.[6] The induced twist depends on the concentration of the chiral guest molecules. The low solubility of many non-mesogenic chiral compounds in a nematic solvent effects that only large pitches can be induced. As a consequence the selective reflexion and the rotatory anomaly occur in the infrared region.

We studied the dependence of the pitch on the temperature as indicated by the center $\tilde{\nu}_R$ of the infrared rotatory anomaly. The measurements can be evaluated with respect to the ordering parameter which has been done for a solution of Brucine (mole-fraction 0.027) in Nematic Phase IV® (eutectic mixture of the isomers of *p*-Methoxy-*p*′-*n*-butylazoxybenzene, purchased from E. Merck, nematic range 16–76°C). The sample thickness is given by the about 26 μm thick lead spacer between NaCl windows. The mean refractive index $n \simeq 1.7$ was obtained using the Fergason equation.[5] Upon increasing temperature we found a monotonous decrease of

a) $\tilde{\nu}_R$ from about 2000 cm^{-1} to 1700 cm^{-1};

b) the amplitude of the rotatory anomaly from 80° to 0, and

c) the width B from about 220 cm^{-1} to 125 cm^{-1}.

Due to Eq. (17) the measured width B allows to evaluate Q directly:

$$Q = \pi\{B^2 - (2nd)^{-2}\}^{1/2}/\tilde{\nu}_R \tag{23}$$

and due to Eq. (22) also the factor sin ε/ε, so that one obtains $Q_0 = Q_1 S$. On the other hand, B was less accurate measured than the amplitude and errors owe a stronger influence due to the difference in Eq. (23). Therefore, these

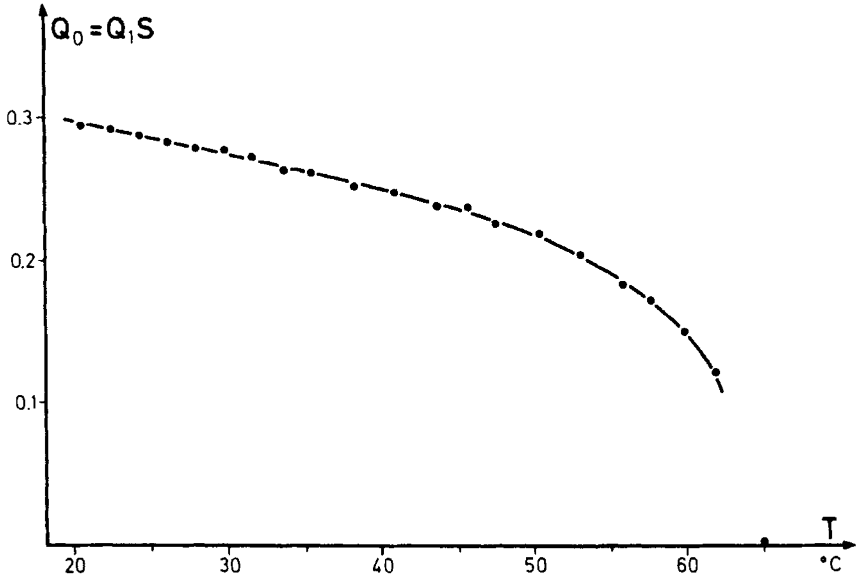

FIGURE 2 Q_0—being proportional to the ordering parameter S—versus temperature for an induced cholesteric solution containing a molefraction $x = 0.027$ Brucine in Nematic Phase IV. Q_0 was evaluated using experimental data of the rotatory anomaly.

results were used only to correct the measured amplitude with respect to the background rotation and to determine the factor $\sin \varepsilon/\varepsilon$. By means of the corrected amplitudes Q_0 was calculated from Eq. (18)

$$Q_0 = Q_1 S = \left\{\left(\frac{A}{90^\circ} + 1\right)^2 - 1\right\}^{1/2} \frac{\pi}{2nd\tilde{\nu}_R} \cdot \frac{\varepsilon}{\sin \varepsilon} \tag{24}$$

The results are shown in Figure 2. Due to the lack of reliable data Q_1 could not be evaluated using Eq. (8).

According to the point of view that the solution mainly consists of nematogenic molecules and is doped only by some guest molecules the highest value of S should be about 0.7, thus leading to $Q_1 \approx 0.42$. Actually, as obvious from Figure 2 the ordering parameter of the cholesteric structure shows a similar decrease upon increasing temperature as known for nematic mesophases.

The variation range of $Q_0 = Q_1 S$ exceeds that reported for nematic liquid crystals. Measurements using other chiral guest compounds seem to show a similar tendency. Structural changes in the vicinity of the clearing temperature or changes of Q_1 and the mean refractive index n as a consequence of the wavenumber shift of the rotatory anomaly might be responsible.

To pursue this problem and to study the orientational order of cholesteric liquid crystals by means of the here defined parameter more previous experiments will be evaluated and improved measurements done.

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