Elastic Constants of Nematic Phenylpyrimidines Determined by Two Different Methods

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A survey of various methods to measure the elastic constants K_i of nematic liquid crystals is given. To determine K_1, K_3 and the anisotropy of the diamagnetic susceptibility $\Delta\chi$ of two members of the 5n-hexyl-2-[4n-alkyloxy-phenyl]-pyrimidines and a mixture of both, we used a combined electro-magneto-optical method, consisting in independent measurements of the optical phase difference in electric and magnetic fields acting on the same cell. The temperature dependence of the K_1- and K_3-values for these phenylpyrimidines can be explained by common theories. The $\Delta\chi$ data show the same temperature dependence as the values of the orientational order parameter S obtained by ^{1}H-NMR.

Key words: Nematic liquid crystals, elastic constants, diamagnetic susceptibility, electro-optic, magneto-optic.

1. Introduction

The interest in accurate measurements of the elastic constants of nematic liquid crystals is very strong. This can be seen from the great number of papers published in the last years, which deal either with experimental techniques for the determination of the elastic constants, or with investigations of these constants for different classes of nematic liquid crystals, homologous series and mixtures.

In the following we list some customary methods for the study of the elastic properties of nematics.

The most wide-spread and elaborate approaches for determination of elastic constants are the optical and capacitive observations of the deformation of the director field in a pre-oriented liquid crystal cell induced by electric [1–10] or magnetic [2, 5, 7, 11–21] fields. These methods have been extensively studied and compared by Gerber and Schadt [22].

Various modifications of these methods can be found in the literature [23–26].

Taking into account deviations from the adiabatic light propagation through a twisted structure, the twist constant has been determined by conoscopic observations [27].

Another technique for the determination of the elastic constants is based upon the analysis of scattered light due to director fluctuations [28–39].

Measurements of the thermal or electrical conductivity of nematics provide elastic constants, too [40, 41].

A direct determination of the twist elastic constant by means of a torque of a thread was proposed by Grupp [42] and Faetti et al. [43].

For the measurements presented in this paper we used an experimental setup that allows to determine the elastic constants of nematic liquid crystals in two different ways. It combines the above mentioned electro-optical and magneto-optical methods.

The external fields and the monochromatic light beam are oriented perpendicular to the surfaces of a planar sandwich cell. The intensity of the light beam passing the cell is recorded as a function of the applied field.

In two separate steps we measured the electrically and magnetically induced optical response of the same cell.

Both fields act independently, and we get two comparable data sets which give use more confidence in the estimation of the error in our results.

The elastic constants K_1 and K_3 were obtained by fitting the continuum equations above the threshold to the optical response of the cell.

Furthermore it is possible to determine, in addition to the elastic constants, the anisotropy $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ of the diamagnetic susceptibility from the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$.

The aim of this paper was the investigation of two members of the 5n-hexyl-2-[4n-alkyloxy-phenyl]-pyrimidines (C_nOPC_6P with $n = 6,9$) and a mixture of

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both Mi3, consisting of 68.5% C_6OPC_6P and 31.5% C_9OPC_6P (see Figure 1).

To prove the reliability of our method, we investigated the well-known nematic 4-[trans-4-pentylcyclohexyl]-benzonitrile (PCH-5), too. This compound was supplied by E. Merck especially for bench-mark tests because of its stability in response to heat, radiation and moisture [44].

2. Experimental

Our experimental arrangement to record the transmitted light intensity as a function of magnetic or electric fields is the same as described elsewhere [4, 12, 20].

The planar liquid crystal cell is placed between crossed polarizers with the initial director axis at 45° to the polarisation axis.

The glass plates are coated with low ohmic In/Sn oxide (ITO) electrodes. The homogeneous planar orientation of the director at the two glass surfaces is obtained by oblique evaporation of a SiO film (about 300 Å) at an angle of about 60° normal to the glasses.

The cell thickness d is typically 40 µm and has been determined interferometrically to $\pm 0.7\%$. We used a sodium-vapour lamp with $\lambda = 589$ nm as monochromatic light source. The transmission was measured by a photomultiplier. The electric field was produced by a programmable sine wave generator at a frequency of about 1 kHz.

The magnetic field was provided by an electromagnet calibrated by means of ^{1}H-NMR with an accuracy better than ± 0.1 mT.

A computer was used to control the fields and to record and store the transmission curve.

The minimum field steps were about 1 mV and 0.1 mT, respectively. The variable sweep rate usually was chosen to be 0.3 mV/s and 0.025 mT/s, respectively.

The cell temperature was controlled to ± 0.1 K.

A suitable region of the cell without dislocations and defects was chosen microscopically prior to the measurements.

The refractive indices n_0 and n_e have been determined using an oriented wedge cell and a goniometer spectrometer with an accuracy of $\pm 0.1\%$ [45].

The dielectric constants parallel and perpendicular to the director ($\varepsilon_{\parallel}, \varepsilon_{\perp}$) were provided by the Halle liquid crystal group [46].

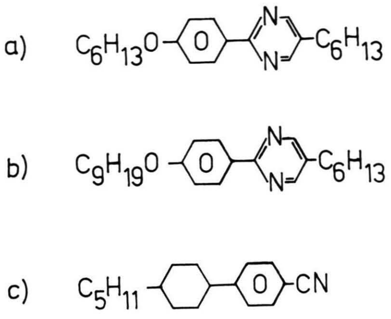

Fig. 1. Chemical structure of the investigated nematic liquid crystals, a) C_6OPC_6P, b) C_9OPC_6P, c) PCH-5.

3. Theory

The reduced intensity I of the transmitted light (ratio of actual to maximum intensity) is a function of the optical phase difference δ between ordinary and extraordinary wave,

$$I = \sin^2\left(\frac{\delta}{2}\right). \tag{1}$$

δ depends on the director configuration and is given by

$$\delta = \frac{2\pi d}{\lambda}\,(\bar{n}_e - n_0) \tag{2}$$

with

$$\bar{n}_e = \frac{1}{d}\int_0^d n_e(z)\,\mathrm{d}z,$$

where z is the direction of light propagation.

At fields f below the threshold field f_c, δ is constant and equal to the initial optical phase difference δ_{init},

$$\delta_{\text{init}} = \frac{2\pi d}{\lambda}\,(n_e - n_0). \tag{3}$$

f stands for E in the electric case and for H in the magnetic experiment.

For the calculation of the elastic constants K_1 and K_3 we used the Deuling procedure [1].

The theoretical expression

$$N_e^{\text{theor}} = \left(\frac{\bar{n}_e}{n_e}\right)^{\text{theor}} = \frac{\int_0^{\pi/2} \frac{F_\eta F_\xi}{F_{-1} F_\nu}\,\mathrm{d}\varphi}{\int_0^{\pi/2} \frac{F_\eta F_\xi}{F_{-1}}\,\mathrm{d}\varphi} \tag{4}$$

with

$$F_\lambda = \sqrt{1 + \lambda \sin^2\theta_M \cdot \sin^2\varphi}; \quad \lambda = \eta,\ \xi,\ \nu,\ -1,$$

and

$$\eta = \frac{K_3}{K_1} - 1,$$

$$\nu = \frac{n_e^2}{n_0^2} - 1,$$

$$\xi = \begin{cases} 0 & \text{(for magnetic deformation)} \\ \dfrac{\varepsilon_{\|}}{\varepsilon_{\perp}} - 1 & \text{(for electric deformation),} \end{cases}$$

is matched to the experimental values $N_e^{\exp}$ at various points by varying θ_M, the angle of maximum deformation in the middle of the cell. The $N_e^{\exp}$ values were sampled at characteristic points of the $I(f)$ curve. In particular we used the extrema of $I(f)$, where $\delta = m\pi$, $m = 1, 2, \ldots$.

The order m was found with the aid of (3). Usually we used the first 5 to 11 extrema at increasing field, corresponding to decreasing interference orders starting from m_{init}.

The relation between θ_M and the field strength is given by

$$\left(\frac{f}{f_c}\right)^{\text{theor}} = \frac{2}{\pi}\sqrt{1 + \xi \sin^2 \theta_M} \int_0^{\pi/2} \frac{F_\eta}{F_{-1} F_\xi} \, d\varphi. \quad (5)$$

The fitting parameters f_c and η were determined by minimization of σ,

$$\sigma = \frac{1}{N} \sum_{j=1}^{N} \sqrt{\left(f_c \left(\frac{f}{f_c}\right)_j^{\text{theor}} - f_j^{\exp}\right)^2} \overset{!}{=} \text{minimum}, \quad (6)$$

where the sum runs over the observed extrema.

From the resulting threshold field f_c we obtain K_1 using

$$K_1 = \frac{U_c^2}{\pi^2} \Delta\varepsilon \, \varepsilon_0, \quad \text{with} \quad U_c = d \cdot E_c, \quad (7\text{a})$$

$$K_1 = \frac{d^2 \cdot B_c^2}{\pi^2 \mu_0} \Delta\chi, \quad \text{with} \quad B_c = \mu_0 H_c. \quad (7\text{b})$$

The constant K_3 is derived from the values of η and K_1.

4. Results and Discussion

The elastic constants K_1 and K_3 of PCH-5 for two temperatures obtained from electric-field measurements are given in Table 1. For the calculation we used the refractive indices and the dielectric constants of [44]. T_c is the clearing temperature.

Table 1. Results of PCH-5; *A*: our investigations; *B*: results of Finkenzeller et al. [44].

$t = T(\text{K})/T_c(\text{K})$	0.925		0.950	
T(°C)	30.3		38.5	
	A	*B*	*A*	*B*
K_1 (pN)	8.2	8.5	7.3	7.3
K_3 (pN)	16.3	16.2	13.3	13.2

The excellent agreement of the data supports the reliability of our measurements.

In order to test additionally our fitting procedure we compared for C_6OPC_6P the fitting parameter U_c with U_c^{graph}, determined graphically from the point of deflection in the optical phase difference curve $\delta = \delta(U)$.

The curve $\delta = \delta(U)$ is easily obtained from the transmission curve $I(U)$ using (1).

The relative differences $\Delta U_c/U_c$ were always less than 0.5%. On the other hand, the deviations between the experimental extrema of the $I(U)$-curve and the corresponding fitted values (compare (6)) were on the average found to be not greater than 0.2%.

The temperature dependence of the elastic constants K_1 and K_3 for C_6OPC_6P, C_9OPC_6P, and Mi3 obtained from electric-field measurements is shown in Figs. 2, 3 and 4.

All elastic constants decrease with increasing temperature. Saupe showed that the elastic constants depend on temperature via the order parameter S and the molar volume V and introduced reduced elastic constants c_i [47]

$$c_i = K_i \frac{V^{7/3}}{S^2} \quad (8)$$

which should be independent of temperature.

Consequently the ratio K_3/K_1 should have no temperature dependence. However, as can be seen in Fig. 5 there exists a weak dependence on temperature.

This weak dependence is in agreement with a large number of published K_3/K_1 data for other compounds [5–7, 12, 13, 15–20] and has been explained by Gruler [13, 48], who assumed changes in short-range order, and by Priest [49], who made the assumption that the elastic constants depend on higher terms of the Legendre polynomials.

A comparison of electric and magnetic measurements without the knowledge of $\Delta\chi$ is possible by analysing the fitting parameters η ($\eta = K_3/K_1 - 1$, see (4)), which are obtained independently. From Fig. 5 a

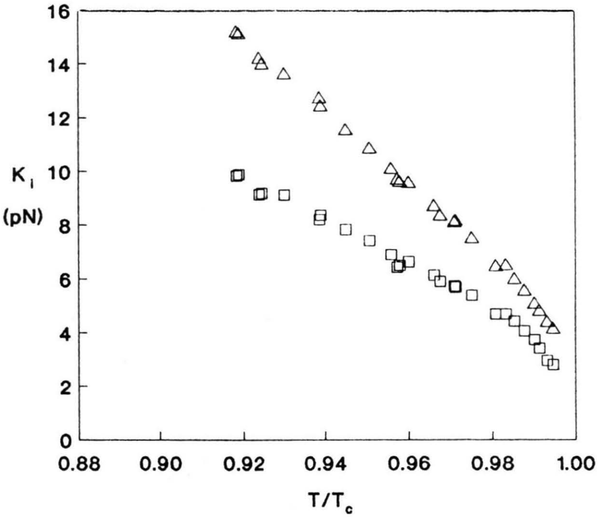

Fig. 2. Temperature dependence of the elastic constants K_1 △ and K_3 □ for C_6OPC_6P.

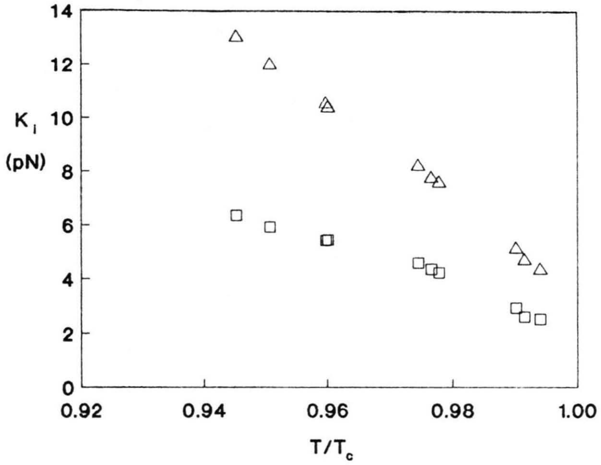

Fig. 3. Temperature dependence of the elastic constants K_1 △ and K_3 □ for C_9OPC_6P.

reasonable agreement between both methods can be seen.

Furthermore we compared the magnitude of the K_3/K_1 values of the measured phenylpyrimidines with similar compounds in the literature. Small K_3/K_1 ratios are typical for compounds with heteroatoms in the rings (as nitrogen or oxygen), like pyrimidines or dioxanes, and with terminal non-polar alkyl chains [18, 50].

The decrease in K_3/K_1 with increasing alkyl chain, as shown in Fig. 6, has been proved for a lot of homologous series [5, 6, 13–15, 51] and is caused by the

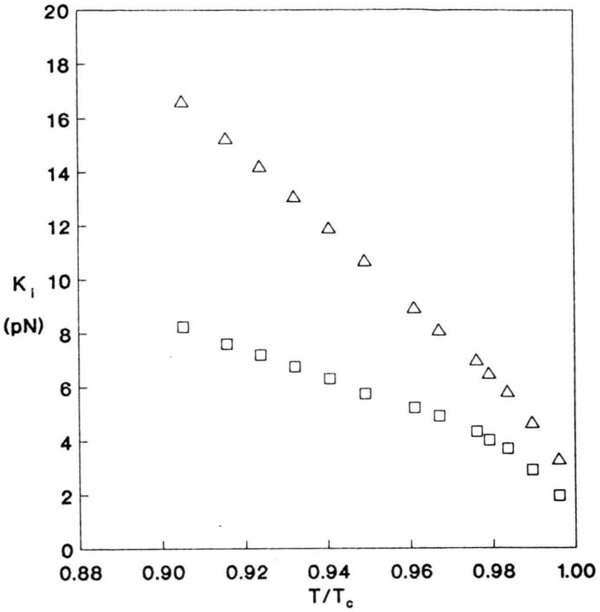

Fig. 4. Temperature dependence of the elastic constants K_1 △ and K_3 □ for Mi3.

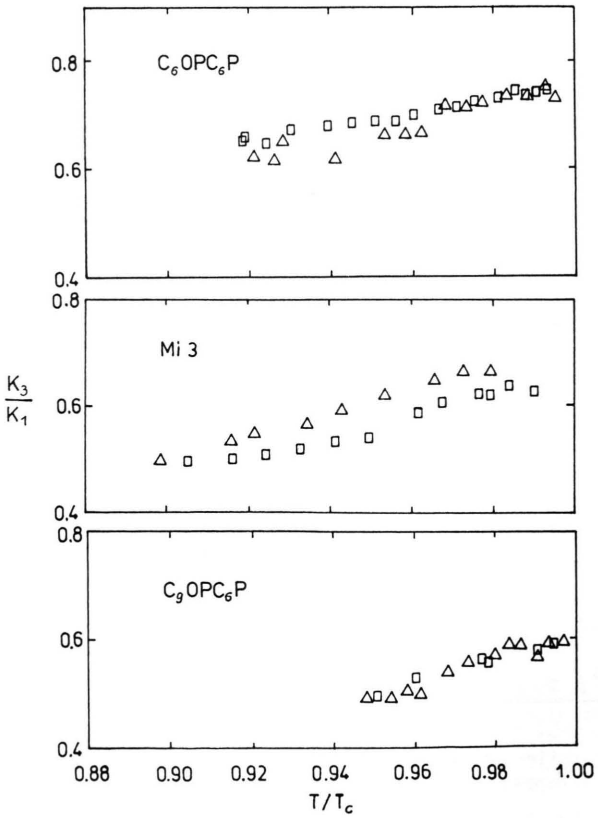

Fig. 5. Temperature dependence of the K_3/K_1-ratio for C_6OPC_6P, C_9OPC_6P and Mi3 measured with electric fields: □ and magnetic fields: △.

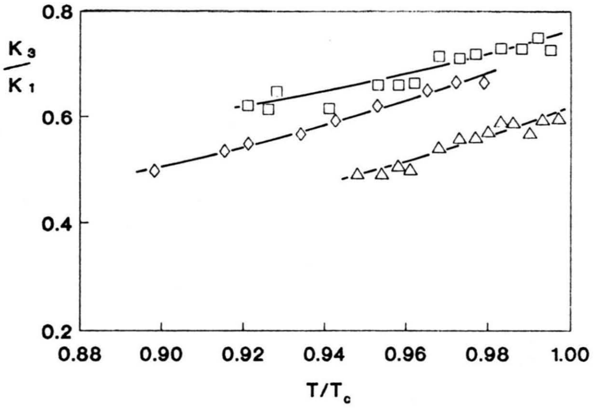

Fig. 6. Temperature dependence of the K_3/K_1-ratio for C_6OPC_6P: □, C_9OPC_6P: △ and Mi3: ◇, measured with magnetic fields.

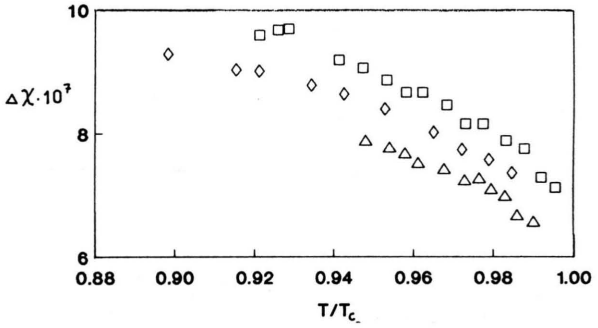

Fig. 7. Temperature dependence of the anisotropy of the diamagnetic susceptibility $\Delta\chi$ for C_6OPC_6P: □, C_9OPC_6P: △ and Mi3: ◇.

increase of smectic-like correlation for longer alkyl chains [52, 53].

The behaviour of Mi3 corresponds to the assumption that the elastic constants of mixtures of similar compounds are linearly related to their molar concentrations [54].

In Fig. 7 we plotted the temperature dependence of the anisotropy of the diamagnetic susceptibility $\Delta\chi$ (volume) obtained from the threshold fields in (7a) and (7b)

$$\Delta\chi = \frac{1}{d^2}\left(\frac{U_c}{B_c}\right)^2 \frac{\Delta\varepsilon}{c^2}, \tag{9}$$

where c is the velocity of light.

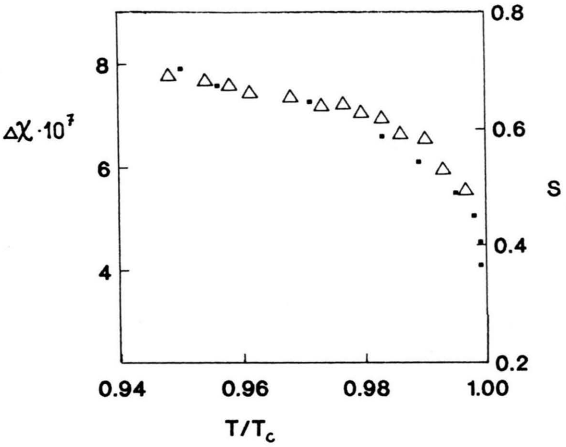

Fig. 8. Dependence on temperature for the anisotropy of the diamagnetic susceptibility $\Delta\chi$: △ and the order parameter S: ■ for C_9OPC_6P.

The absolute values of $\Delta\chi$ are relatively small. However one can see from Fig. 7 that $\Delta\chi$ decreases for increasing alkyl chain length. This behaviour is in agreement with $\Delta\chi$ measurements of PCH in [5].

In Fig. 8 we fitted for C_9OPC_6P the $\Delta\chi(T/T_c)$-curve to the temperature dependence of the order parameter S. The values of S were determined by ^{1}H-NMR previously in our group [55].

$\Delta\chi$ is related to the order parameter S by

$$\Delta\chi = \chi_0 \cdot S. \tag{10}$$

We obtained $\chi_0 = 10.4 \cdot 10^{-7}$, using linear regression.

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