Diamagnetic anisotropy and rotational viscosity of 6CHBT nematic liquid crystal

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Abstract. Nematic liquid crystal with polar terminal NCS group was studied by using acoustic and electro-optical methods. Experimental results on rotational viscosity have been obtained by two methods. The anisotropy of diamagnetic susceptibility of the studied LC with temperature variation was determined based on the comparison of these methods. The present results may be useful for testing physical models of the orientation dynamics of nematic liquid crystals in alternating electric and magnetic fields.

1. Introduction

Nematic liquid crystals (NLC) with high birefringence $\Delta n$ and low viscosity are particularly attractive for displays, infrared and microwave applications \[1-7\]. The birefringence of NLC is mainly determined by the length of $\pi$-conjugation, molecular shape, functional and terminal groups. The presence of benzene rings as well as double and triple bonds lead to highly conjugated compounds \[8\]. The main drawbacks of this highly conjugated structures for practical applications are usually high melting point and strong smectogenic character. The addition of a terminal nitrogen-containing group make it possible to achieve ultra-high birefringence. Isothiocyanates (compounds with polar terminal NCS groups) have the highest birefringence among such materials \[9\]. Isothiocyanates, as compounds with high $\Delta n$, seem to be more suitable for application than other polar ones due to their lower bulk and rotational viscosities. The latter is lower by up to 35% than for structurally comparable CN compounds \[10\].

It is also known that the influence of ultraviolet (UV) radiation adversely affects operational parameters of LC materials: clearing point, birefringence, dielectric permittivity, as well as viscous and elastic constants. However, the addition of nitrogen containing groups increases UV resistance, and isothiocyanates have the highest stability among appropriate structures of other polar groups \[11\].

Experimental studies of the influence of alternating electric and magnetic fields on the orientation structure of liquid crystals allow us to obtain information about the relaxation, elastic and viscous properties \[12\]. In the present work the rotational viscosity of NLC with
Figure 1. The structural formula of 6CHBT

Figure 2. Thermogram of 6CHBT

polar terminal NCS group is measured using the Bogdanov method [13] and electro-optical method [14,15] with temperature variation. The approach used, based on the comparison of the two methods, allows us to determine the anisotropy of diamagnetic susceptibility of the studied LC.

2. Materials and Methods

2.1. Materials

In this paper we present the results of rheological measurements of nematic liquid crystal 1-(4-hexyl-cyclohexyl)-4-isothiocyanato-benzene (6CHBT, Military Technical University, Warsaw, Poland) with polar terminal NCS group. The structural formula of 6CHBT is shown in Fig. 1.

According to literature data 6CHBT has a melting point of $T_{Cr-N} = 285.7$ K and a clearing point of $T_{N-Iso} = 316.7$ K [16]. It was found, using differential scanning calorimetry (Mettler Toledo DSC 3) and polarizing light microscopy (Altami Polar 3), that phase transition temperatures of the studied LC correspond to these data. The measurements were carried out using standard aluminum crucibles with a volume of 40 µl in the heating and cooling mode from 183 to 383 K with a rate of 33 mK/s. The temperature of the sample was kept at a constant temperature for at least 30 minutes for every measurement. The resulting thermogram is shown in Fig. 2.
2.2. Electro-optical response
The electro-optical properties of 6CHBT were studied using a standard technique based on the
determination of the volt-contrast performance of a planar NLC cell [17, 18]. A continuous
sinusoidal signal with a frequency of 5 kHz was applied to the cell. The signal cycle in this case
is much less than both the director reorientation time and the relaxation time of ionic charges.
Under these conditions, the director does not respond to the fluctuations of the electric field, but
is sensitive to its RMS value. The amplitude of the alternating signal ranged from 0 to 80 V. A
linearly polarized helium-neon laser ($\lambda = 632.8$ nm) was chosen as a light source. A planar LC
cell is placed between crossed polarizers so that the angle between the director and the allowed
orientation of each of the polarizers is ±45°. After passing through the cell, the optical signal
reaches a photodiode; it is amplified and registered by an automatic recorder. Together with
the intensity of the transmitted laser radiation, the recorder simultaneously registers the signal
being supplied from the generator to the cell.

The dynamic parameters of the electro-optical response were studied using the S-Recorder
L recording voltmeter with a sampling rate of 100 kHz. Instead of a continuous signal, an
amplitude-modulated signal of the same frequency with an interval between bursts of 500 ms
and a duration of 100 ms is supplied to the cell. The amplitude of the test signal was 5 V. The
rising $\tau_{on}$ and the decay $\tau_{off}$ times were determined analyzing the change in the phase delay
$\Delta \Phi$ from 10% to 90% of the maximum value for a specified voltage and from 90% to 10%,
respectively.

Rotational viscosity is calculated from the experimental data of the decay time according to
the formula [19, 20]
\[
\gamma_1 = \frac{\tau_{off} U_{th}^2 \varepsilon_0 \Delta \varepsilon}{d^2},
\]
where $U_{th}$ is a threshold voltage of the Freedericksz transition, $\Delta \varepsilon$ is a dielectric permittivity
anisotropy, $\varepsilon_0$ is an electric constant, $d$ is a thickness of the liquid-crystal layer.

Experimental data on the temperature dependence of the dielectric permittivity anisotropy
of 6CHBT were taken from [21].

2.3. Acoustic implementation of the rotating magnetic field method
The acoustic method of Bogdanov [13] was developed to measure the rotational viscosity
of nematic liquid crystals in a rotating magnetic field by the phase diagram of the angular
dependence of the ultrasonic absorption. This method clearly shows the existence of rotational
viscosity without additional processing of experimental data [22–26].

The pulse ultrasonic method with a fixed distance between piezoelectric transducers is used
to determine the acoustic properties of LC. The rotating magnetic field is formed by a permanent
magnet, which is fixed on a rotating platform. The platform rotation frequency can be varied
in the range of $f_H = 0.056 – 280$ mHz. The magnetic field strength is 110 kA/m. The acoustic
chamber is fixed between the poles of a permanent magnet. The chamber is a nonmagnetic
tin bronze cylinder with a length of $l = 11$ mm and a diameter of $D = 11$ mm. Piezoelectric
transducers from lead zirconate titanate (PZT) with a resonant frequency of 4.2 MHz are glued
to the ends of this cylinder.

The measurements of the amplitude of the probe pulse were carried out using an automatic
recorder S-Recorder L, while the second channel of the device received control marks from the
photodiode every 90° during the rotation of the platform. The initial displacement of the acoustic
chamber $\psi_0$ as well as the lag angle of the director $\psi$ is determined by the control marks from
the photodiode. Then the angular dependence of the ultrasonic absorption coefficient changes
$\Delta \alpha(\varphi) = \alpha(\varphi) - \alpha(90°)$ is determined. The signal frequency was set to $f_0 = 4.2$ MHz and
corresponded to the main resonance of the piezoelectric transducer. The amplitude of the
voltage applied was 15 V.
3. Results and discussion

The expression for $\Delta \alpha (\varphi)$ in the case of longitudinal waves propagating in the NLC at an angle $\varphi$ to the director according to the Ericksen-Leslie theory has the form [27–29]

$$\Delta \alpha = \frac{\omega^2}{2\rho c_0^2} \left( a \cos^2 \varphi + b \cos^4 \varphi \right),$$

where $a, b$ are numerical coefficients, that have dimension of viscosity, $c_0$ is a low-frequency limit of the speed of sound, $\rho$ is a density of the NLC, $\omega$ is a circular frequency of the ultrasonic wave.

Figure 3a shows the phase lag $\psi$ of the director and the magnetic field strength vector at $\Omega = 52.4 \, \text{rad/s}$ and $T = 295 \, \text{K}$. The solid lines are best fits to expression (2). The phase difference $\psi$ between the external field and director orientation is a consequence of the presence of a torque acting on the molecular director in a rotating magnetic field. The torque experienced by the liquid crystal sample in this case is $M = \Delta \chi \mu_0 H^2 V \sin 2\psi/2$, where $\mu_0$ is a vacuum permeability.

The equality of the moment of friction and the magnetic moment corresponds to a steady rotation

$$\gamma_1 V \Omega = \frac{\Delta \chi \mu_0 H^2 V \sin 2\psi}{2},$$

A steady rotation of the liquid crystal is possible only at frequencies

$$\Omega \leq \frac{\Delta \chi \mu_0 H^2}{2\gamma_1} = \Omega_0.$$

Figure 3b shows the experimental curves $\sin 2\psi$ vs $\Omega$, which are satisfactorily described by expressions (3) and (4). The reason for the deviation of the experimental data from the theoretical predictions at large $\Omega$ is the inhomogeneities in the orientation of the sample caused by vortices. Thus, reliable data can only be obtained for sufficiently small $\Omega$. 
The critical frequency $\Omega_0$ of the synchronous mode is determined by the experimental values of the $\sin 2\psi$. Then, the ratio of the rotational viscosity to diamagnetic susceptibility anisotropy $\gamma_1/\Delta\chi$ is calculated according to the expression

$$\frac{\gamma_1}{\Delta\chi} = \frac{\mu_0 H^2}{2\Omega_0}. \quad (5)$$

The temperature dependence $\gamma_1/\Delta\chi$ shown in Figure 4a can be used to determine the anisotropy of diamagnetic susceptibility. For this purpose, the electro-optical response of a thin layer of 6CHBT liquid crystal was studied. It is possible to calculate the temperature dependence of the anisotropy of diamagnetic susceptibility (Figure 4b) by comparing the experimental data obtained by electro-optical and acoustic methods.

Diamagnetic anisotropy of liquid crystals is determined by two factors: the structure and orientation of the molecules [30]. It is known that the magnetic anisotropy of aromatic compounds is mainly determined by the anisotropy of the benzene rings. Despite the fact that a liquid crystal can be considered macroscopically homogeneous under experimental conditions, the axes of its molecules deviate from the equilibrium position at significant angles due to thermal fluctuations. Therefore, diamagnetic anisotropy decreases with increasing temperature. The orientation order parameter is defined by the degree of alignment of the molecules $S = \Delta\chi/\Delta\chi_0$, where $\Delta\chi_0$ is a diamagnetic anisotropy at $T = 0$ K [31]. It can be determined from the experimental dependence $\Delta\chi(T)$ as follows [32,33]

$$\Delta\chi = \Delta\chi_0 S = \Delta\chi_0 \left(1 - \frac{T}{T_{N-Iso}}\right)^\beta, \quad (6)$$

where $\beta$ is a numerical parameter.

The solid lines in Figure 4b stand for the fitted curves using (6). The values of the order parameter obtained using the Bogdanov method and dielectric spectroscopy [21] are in good agreement. The behavior of the temperature dependence of the order parameter is well described by the expression (6).

Figure 4. Temperature dependence of a) the $\gamma_1/\Delta\chi$ ratio and b) the orientation order parameter $S$. 

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Conclusions
The combination of the well-known electro-optical method with the rotating magnetic field method provides extensive information on the rheological, magnetic and orientational properties of nematic liquid crystals. The temperature dependences of the rotational viscosity, the diamagnetic susceptibility anisotropy, and the orientation order parameter of NLC with polar terminal NCS group were obtained. The results obtained are in good agreement with the literature data. The acoustic method of Bogdanov may be of interest for setting up experiments with complex configurations of alternating magnetic and electric fields, as well as for studying the structural and relaxation features of liquid crystals under high pressure.

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