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## Dielectric Relaxation of *trans*-4-Propyl-(4-Cyanophenyl)-Cyclohexane Liquid Crystals

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**Abstract**—The frequency dependences of the permittivity of a *trans*-4-propyl-(4-cyanophenyl)-cyclohexane (3PCH) liquid crystal in the nematic phase are measured in the frequency range 1–2000 MHz for different orientations of the director of liquid-crystal molecules with respect to the polarization of an ac electric field. The temperature dependences of the dielectric and optical characteristics are compared in the range of the transition from the nematic phase to the isotropic liquid phase. The dielectric spectra are approximated numerically, and the times of dipole relaxation upon rotation of the molecules about the short and long axes are determined. It is demonstrated that intramolecular motions make a significant contribution to the relaxation. The activation enthalpies are calculated. © 2004 MAIK “Nauka/Interperiodica”.

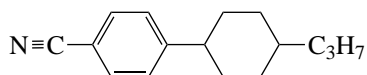
### 1. INTRODUCTION

It is known that the difference between static permittivities of nematic liquid crystals with parallel  $\epsilon_{\parallel 0}$  and perpendicular ( $\epsilon_{\perp 0}$ ) orientations of the director of liquid-crystal molecules with respect to the electric pump field is associated with rotations of the molecules about the short and long molecular axes [1]. As a rule, the frequency dependences of the longitudinal (parallel)  $\epsilon_{\parallel}(f)$  and transverse (perpendicular)  $\epsilon_{\perp}(f)$  permittivities are adequately described by the Debye equations with relaxation times  $\tau_{\parallel}$  and  $\tau_{\perp}$ , which can differ from each other by several orders of magnitude. It is worth noting that the Debye relaxation time for molecules of many liquid crystals in an isotropic state approximately coincides with the relaxation time  $\tau_{\perp}$ . The frequency dependence of the longitudinal permittivity  $\epsilon_{\parallel}(f)$  of liquid crystals in the nematic phase is considerably shifted to the low-frequency range due to the interaction of liquid-crystal molecules, which is responsible for the formation of the potential barrier to rotations of the molecules about the short axis [1, 2].

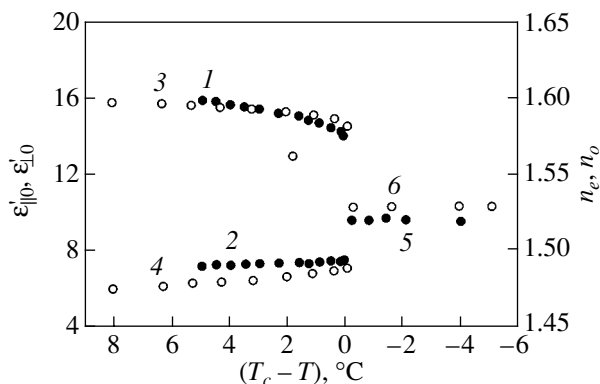
However, the experimental dielectric spectra of liquid crystals measured over a wide range of frequencies are often characterized by noticeable deviations from the Debye behavior due to the contributions from additional relaxation mechanisms associated, for example, with intramolecular motions. In particular, this is characteristic of the dielectric spectra of liquid crystals belonging to the alkylcyanobiphenyl group *n*CB ( $n = 5–9$ ). Molecules of these compounds contain a rigid aromatic core and an alkyl tail consisting of conformationally mobile methylene fragments. It should be noted that the dielectric spectra of the aforementioned liquid crystals significantly deviate from the Debye behavior in high- and ultrahigh-frequency ranges for perpendic-

ular orientations of the director of molecules with respect to the polarization of the electric pump field [3–6]. The observed deviations are associated with the induced polarizability of the alkyl chains due to a change in their conformational equilibrium in microwave electric fields. The greater the number of methylene groups in liquid-crystal molecules, the more widely the frequency dependence of the real part of the transverse permittivity  $\epsilon'_{\perp}(f)$  deviates from the Debye behavior, because the number of overlapping ranges of natural frequencies of characteristic conformational vibrations increases and, correspondingly, their frequency range becomes wider.

Earlier [7], we showed that the frequency dependence of the real part of the transverse permittivity  $\epsilon'_{\perp}(f)$  for *n*CB liquid crystals ( $n \geq 5$ ) can be numerically approximated to a high accuracy by the Debye dispersion relation with a continuous distribution of relaxation times in a specified range. This distribution is adequately described by an asymmetric function. However, within the proposed approach, it is impossible to separate and identify the contributions from different molecular motions to the relaxation processes and to determine the relaxation times associated with the motion of the aromatic core and the flexible terminal fragments of the molecules. With a decrease in the number of methylene groups to  $n = 3$  in the alkyl tail, for example, for a 5-propyl-2-(*p*-cyanophenyl)-pyridine liquid crystal, the dielectric spectrum  $\epsilon'_{\perp}(f)$  can be well approximated using the Debye dispersion relation with a symmetric continuous distribution function of relaxation times in a relatively narrow range  $(23.9–1.85) \times 10^{-9}$  s [8]. In this case, fluctuations of chain bending due to internal rotations of fragments in the



**Fig. 1.** Structural formula of the *trans*-4-propyl-(4-cyanophenyl)-cyclohexane liquid-crystal compound.



**Fig. 2.** Temperature dependences of the optical  $n_e$  and  $n_o$  (closed symbols) and dielectric  $\epsilon'_{\parallel 0}$  and  $\epsilon'_{\perp 0}$  (open symbols) parameters for the 3PCH liquid crystal in the temperature range of the transition from the nematic phase to the isotropic liquid phase (for explanation of the curves, see text).

alkyl tail can be considered to be statistically independent [9], because the distribution functions of their natural frequencies virtually do not overlap with each other.

In the present work, we measured and analyzed the dielectric spectra of a monotropic liquid crystal, namely, *trans*-4-propyl-(4-cyanophenyl)-cyclohexane (3PCH), with a short alkyl tail ( $n = 3$ ). The structural formula of the *trans*-4-propyl-(4-cyanophenyl)-cyclohexane liquid-crystal compound is presented in Fig. 1. The monotropic properties of the 3PCH liquid crystal manifest themselves in the fact that this compound undergoes a transition to the liquid-crystal phase at a temperature  $T_c = 46^\circ\text{C}$  only from the isotropic phase formed upon preliminary heating of the compound to temperatures  $T > T_c$ . The crystallization temperature of the 3PCH compound ( $T \leq 36^\circ\text{C}$ ) depends on the cooling rate. The purpose of this work was to separate the contributions from different rotational (reorientational) molecular and intramolecular motions to the frequency dependences of the permittivities of the 3PCH liquid crystal. The dielectric spectra were measured over a wide frequency range ( $f = 1\text{--}2000$  MHz) at several fixed angles  $\varphi$  between the director of liquid-crystal molecules and the polarization of the microwave pump field. The experimental temperature dependences of the permittivities and refractive indices were obtained in the temperature range of the phase transition from the nematic liquid crystal to the isotropic liquid.

Investigation into the optical and dielectric properties of the 3PCH nematic liquid crystal is of particular interest, because this compound is similar in molecular structure to the well-known and thoroughly studied liquid crystals of the alkylcyanobiphenyl group  $n\text{CB}$  ( $n = 5\text{--}9$ ) [3–7]. The only difference between them lies in the fact that, in the rigid core of the 3PCH molecule, one benzene ring is replaced by a cyclohexane fragment. Moreover, the number of methylene fragments ( $n = 3$ ) in the alkyl tail of the 3PCH molecule is rather small for liquid crystals and equal to that for a 5-propyl-2-(*p*-cyanophenyl)-pyridine liquid crystal [8]. However, unlike the pyridine-containing liquid-crystal compound, the 3PCH nematic liquid crystal is characterized by a permanent dipole moment associated with the presence of the  $\text{--C}\equiv\text{N}$  group and directed along the long molecular axis.

## 2. EXPERIMENTAL TECHNIQUE

The permittivities of the 3PCH nematic liquid crystal were measured with the use of capacitive and special microstrip sensors. The sensor design, equipment, and technique of measurements were thoroughly described in our previous works [10, 11]. The absolute errors in determining the dielectric characteristics were no larger than  $\delta\epsilon' \sim 0.05$  and  $\delta\epsilon'' \sim 0.1$ . The required angle  $\varphi$  between the long axes of molecules in the 3PCH sample and the polarization of the microwave electric field in the measuring cell was specified by the appropriate direction of the static magnetic field  $H = 2500$  Oe. The dielectric spectra were recorded at a temperature  $T = T_c - 5^\circ\text{C}$ . In order to calculate the activation enthalpies upon longitudinal and transverse pumping of the sample, the dielectric spectra were measured at a temperature  $T = T_c - 10^\circ\text{C}$ . The measurements of the static permittivities were performed at temperatures of  $30\text{--}60^\circ\text{C}$  and a frequency of 1 MHz, at which the dispersion is virtually absent. The temperature was maintained accurate to  $\pm 0.5^\circ\text{C}$ .

The temperature dependences of the ordinary ( $n_o$ ) and extraordinary ( $n_e$ ) refractive indices were measured at the wavelength  $\lambda = 0.589$   $\mu\text{m}$  with the use of an IRF-454B refractometer with a homeotropic orientation of the director in the measuring cell. These data were required for the numerical approximation of the dielectric spectra.

## 3. RESULTS AND DISCUSSION

The experimental temperature dependences of the extraordinary  $n_e$  (closed symbols 1) and ordinary  $n_o$  (closed symbols 2) refractive indices for the nematic phase and the temperature dependence of the refractive index for the isotropic phase (closed symbols 5) are depicted in Fig. 2. This figure also shows the temperature dependences of the real parts of the longitudinal  $\epsilon'_{\parallel}$  (open symbols 3) and transverse  $\epsilon'_{\perp}$  (open symbols 4)

permittivities of the 3PCH nematic liquid crystal, which were measured in parallel and perpendicular orientations of the director of liquid-crystal molecules with respect to the electric pump field. The temperature dependence of the permittivity for the isotropic phase is represented by open symbols 6. In this case, the cooling rate of the sample was approximately equal to 4 K/h. It can be seen from Fig. 2 that the measured parameters only slightly depend on the temperature in both the nematic (curves 1–4) and isotropic (curves 5, 6) phases. It is worth noting that the optical anisotropy is relatively small:  $\Delta n = n_e - n_o \approx 0.11$ .

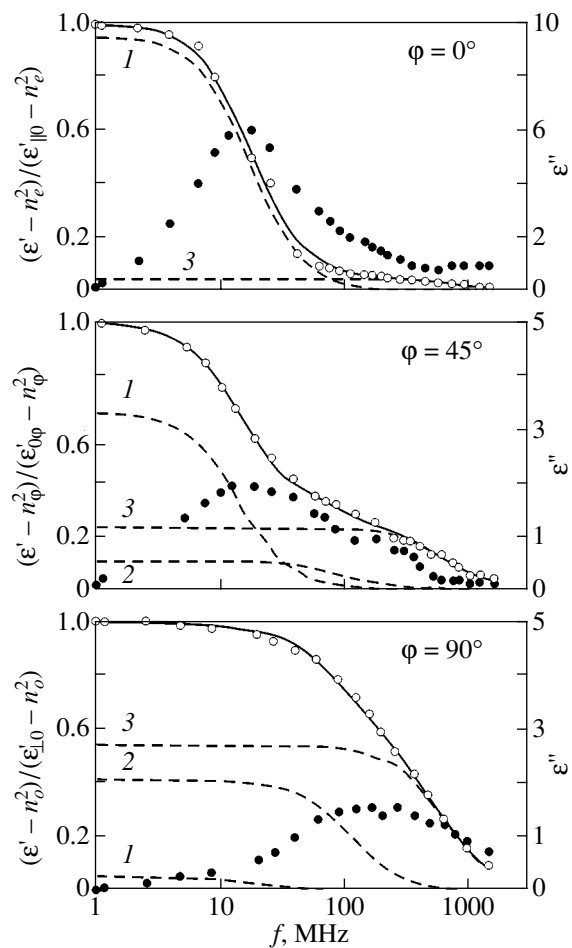
The frequency dependences of the real and imaginary parts of the permittivity of the 3PCH liquid crystal in the nematic phase were measured for the following angles between the director of liquid-crystal molecules and the polarization of the electric pump field:  $\varphi = 0^\circ, 10^\circ, 20^\circ, 45^\circ, 70^\circ, 80^\circ,$  and  $90^\circ$ . The dielectric spectra  $\varepsilon'_\varphi(f)$  were numerically approximated by the sum of three Debye processes with different relaxation times  $\tau_1, \tau_2,$  and  $\tau_3$ ; that is,

$$\frac{\varepsilon'(f) - n_\varphi^2}{(\varepsilon'_{0\varphi} - n_\varphi^2)} = \sum_{i=1}^3 \frac{g_i}{1 + 4\pi^2 f^2 \tau_i^2}, \quad (1)$$

where  $n_\varphi = n_e \cos^2 \varphi + n_o \sin^2 \varphi$ ,  $\varepsilon'_{0\varphi}$  is the static permittivity at a given angle  $\varphi$ , and  $g_i$  are the weighting factors ( $g_1 + g_2 + g_3 = 1$ ). It is assumed that the first two terms in expression (1) characterize the rotation (reorientation) of molecules about the short and long axes, respectively, and the third term describes the conformational motion of methylene groups in the alkyl tail. It is evident that, within this approach, the quantity  $\tau_3$  is the mean (or most probable) relaxation time for all conformational motions in the alkyl tail.

Figure 3 shows the frequency dependences of the normalized real permittivity  $\varepsilon'(f)$  (open symbols) and the magnitude of the imaginary permittivity  $\varepsilon''(f)$  (closed symbols) measured at angles  $\varphi = 0^\circ, 45^\circ,$  and  $90^\circ$ . In this figure, solid lines represent the results of the numerical Debye approximation of these dependences according to expression (1) and dashed lines 1–3 correspond to individual contributions from the three aforementioned relaxation processes to the total dispersion of the permittivity. It should be noted that the frequency dependence of the permittivity calculated within the proposed approximation is in good agreement with the experimental data obtained for all the director orientations over the entire frequency range covered.

As could be expected, at  $\varphi = 0^\circ$ , the dielectric spectrum  $\varepsilon'(f) = \varepsilon'_\parallel(f)$  in the low-frequency dispersion region is predominantly determined by the rotation of molecules about the short molecular axis ( $g_1 = 0.95$ ,  $\tau_1 = 9$  ns). The activation enthalpy  $\Delta H_1 = 72 \pm 4$  kJ/mol was calculated from the temperature dependence of the relaxation time  $\tau_1(T)$ . This value is characteristic of the reorientation of liquid-crystal molecules about the short



**Fig. 3.** Frequency dependences of the real (open symbols) and imaginary (closed symbols) permittivities of the 3PCH liquid crystal for different orientations of the director of the liquid-crystal molecules. Solid lines correspond to the Debye approximations. Dashed lines 1–3 indicate the contributions from three relaxation mechanisms (for explanation of the curves, see text).

axis in the nematic phase. Moreover, the dielectric spectrum in the high-frequency dispersion region is characterized by a small contribution from the conformational motions of the alkyl tail ( $g_3 = 0.05$ ,  $\tau_3 = 0.2$  ns). However, for this director orientation, the rotation of molecules about the long axis does not contribute to the dispersion of the longitudinal permittivity  $\varepsilon'_\parallel(f)$  ( $g_2 = 0$ ).

It can be seen from Fig. 3 that, at  $\varphi = 45^\circ$ , the dielectric dispersion contains contributions from all three relaxation processes under consideration. The weighting factors of these processes are of the same order of magnitude ( $g_1 = 0.66$ ,  $g_2 = 0.11$ ,  $g_3 = 0.23$ ). Note that the contribution from the rotation of molecules about the long axis (relaxation time  $\tau_2 = 1.4$  ns) is maximum, whereas the contribution from the rotation of molecules about the short axis is minimum. At  $\varphi = 90^\circ$ , the dielectric spectrum  $\varepsilon'(f) = \varepsilon'_\perp(f)$  should also be approxi-

Main characteristics of the liquid crystal for different orientations of the polarization of a microwave electric field with respect to the director of molecules

$\varphi$ , deg	$\tau_1$ , ns	$\tau_2$ , ns	$\tau_3$ , ns	$g_1$	$g_2$	$g_3$	$n$	$\epsilon_0$
0	9	–	0.20	0.95	0	0.05	1.600	15.69
10	8	–	0.25	0.90	0	0.10	1.597	13.70
20	8	–	0.25	0.90	0	0.10	1.596	12.50
45	11	1.56	0.23	0.66	0.11	0.23	1.545	9.57
70	13	1.40	0.25	0.35	0.30	0.35	1.503	7.55
80	10	1.41	0.24	0.10	0.44	0.46	1.493	6.10
90	8	1.40	0.25	0.05	0.41	0.54	1.490	6.05

mated with allowance made for all three relaxation processes. In this case, the contribution from the reorientation of molecules about the short axis decreases significantly ( $g_1 = 0.05$ ). Although the contributions from the other two mechanisms are comparable in magnitude ( $g_2 = 0.41$ ,  $g_3 = 0.54$ ), the contribution from the conformational motion of the alkyl tail appears to be dominant. This is a rather unexpected result; nonetheless, it accounts for the fact that the dielectric spectra  $\epsilon'_\perp(f)$  noticeably deviate from the Debye behavior in the high-frequency range.

It should be noted that, like the time of longitudinal relaxation  $\tau_1$ , the time of transverse relaxation  $\tau_2$  is a function of the temperature. However, the activation enthalpy calculated from the temperature dependence  $\tau_2(T)$  proves to be substantially less:  $\Delta H_2 = 9 \pm 2$  kJ/mol. For the nematic liquid-crystal phase, the relaxation time  $\tau_3$  does not depend on the temperature in the range studied.

The table presents the relaxation times, weighting factors, refractive indices, and static permittivities of the liquid crystal under investigation for different orientations of the director of liquid-crystal molecules with respect to the polarization of the electric pump field. It can be seen from the table that the relaxation times only weakly depend on the angle  $\varphi$ . However, the relaxation time  $\tau_1$  reaches a maximum at  $\varphi \approx 70^\circ$ , whereas the maximum value of  $\tau_2$  is observed at  $\varphi \approx 45^\circ$ . This suggests that weak relaxation processes manifest themselves at particular angles  $\varphi$  and hinder the reorientation of molecules about the long and short axes. The relaxation time  $\tau_3$  can be considered to be virtually independent of the angle  $\varphi$ .

#### 4. CONCLUSIONS

Thus, the permittivities of the *trans*-4-propyl-(4-cyanophenyl)-cyclohexane liquid-crystal compound were measured over a wide frequency range for different orientations of the director of liquid-crystal molecules with respect to the polarization of the electric field. The dielectric spectra were numerically approximated using the sum of three Debye processes with different relaxation times. The proposed approximation of the dielectric spectra  $\epsilon'(f)$  made it possible to reveal important features in the dependence of the ratio of the contributions from three dominant mechanisms of relaxation in the liquid crystal (rotations of molecules about the short and long molecular axes and intramolecular conformational motions of the alkyl tail of the 3PCH molecule) on the angle  $\varphi$  between the polarization of the electric pump field and the director of the liquid-crystal molecules. However, the approximation approach used in our consideration offers an adequate description only for molecules with a small number  $n$  of methylene fragments in the alkyl tail in the case where the real distributions of relaxation times do not overlap in the vicinity of  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ . As the number of methylene groups in the alkyl tail of liquid-crystal molecules increases ( $n > 3$ ), the range of relaxation times corresponding to intramolecular motions becomes wider and, therefore, the parameter  $\tau_3$  as an effective relaxation time loses its meaning. In this case, the dielectric spectra can be well approximated by the Debye dispersion relation with an asymmetric continuous distribution function of relaxation times in a specified range.

The above investigations demonstrated that the intramolecular motions in liquid crystals slightly affect the dispersion of the longitudinal permittivity  $\epsilon'_\parallel(f)$ , even though it is determined primarily by rotations of molecules about the short axis. At the same time, rotations of the molecules about the long axis do not contribute to the dispersion of the longitudinal permittivity. It was also established that the dispersion of the transverse permittivity  $\epsilon'_\perp(f)$  is governed by the contributions from all three relaxation mechanisms; however, the greatest contribution in this case is made by intramolecular motions.

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