Dielectric Relaxation Studies of 5PCH by the Time Domain Spectroscopy Method

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The time domain spectroscopy (TDS) method has been used for the measurement of the complex dielectric permittivity in the isotropic phase and for perpendicular and parallel orientations in the nematic phase of 5PCH (4-(*trans*-4-pentyl-cyclohexyl)-benzonitrile). The accessible frequencies range from ca 15 MHz to ca. 1.5 GHz. The obtained spectra are well consistent with the spectra measured recently in the frequency domain (T. Brückert et al., Mol. Cryst. Liq. Cryst., in press). From the relaxation times $\tau_{\parallel}$, $\tau_{\perp}$ and τ_{is} we have calculated the activation enthalpies and the retardation factors $g_{\parallel}$ and $g_{\perp}$ that allow to obtain the nematic potential q. The validity of some assumptions of the mean-field theories of the nematic state are discussed.

Key words: Liquid crystals, 4-(*trans*-4-pentyl-cyclohexyl)-benzonitrile (5PCH), dielectric relaxation, time domain spectroscopy.

Introduction

Measurements of the dielectric permittivity, ε', and loss, ε'', give information about the dynamic behaviour of dipolar molecules, in condensed phases. Dielectric relaxation processes in liquid crystals (LC) depend on molecular structure, intermolecular interactions and degree of molecular order. One can distinguish two main processes: molecular reorientations around the short and long axes. They are well separated in the frequency scale: the first is found at radio frequencies (low frequency, l.f., process), whereas the second one reaches gigahertz frequencies (high frequency, h.f., process) [1–5]. Moreover, the l.f. process is well seen for parallel orientation ($\boldsymbol{E} \parallel \boldsymbol{n}$, $\boldsymbol{E}$ – measuring electric field, $\boldsymbol{n}$ – director), and the h.f. one for perpendicular orientation of a LC sample ($\boldsymbol{E} \perp \boldsymbol{n}$). In the isotropic phase both processes merge, giving one broad relaxation spectrum. The wide frequency range means that different experimental techniques have to be used to study all the processes.

Usually the dielectric measurements are limited to ca. 10 MHz (e.g. [1, 6]), although measurements up to a few GHz are also reported (e.g. [2, 3]). The time domain spectroscopy technique (TDS) has been applied to study LC's in a few cases only [4, 5, 7, 8]. TDS spectra, after transformation to the frequency domain, can cover frequencies from ca. 10 MHz to ca. 10 GHz. The TDS method is especially suited for studying the h.f. process in the nematic phase as well as the processes occurring in the isotropic phase. However, the high frequency wing of the l.f. process can also be detected.

In this paper we report on TDS measurements carried out on 4-(*trans*-4-pentyl-cyclohexyl)-benzonitrile (5PCH) in the nematic and isotropic phases. The relaxation spectra were measured for parallel and perpendicular orientation of the nematic phase. The results are confronted with the spectra recently obtained in frequency measurements [6].

The obtained results allow us to calculate the relaxation times $\tau_{\parallel}$, $\tau_{\perp}$, and τ_{is} as function of temperature. Using the Arrhenius equation, the corresponding activation barriers were estimated. Additionally, the extrapolation of the relaxation time τ_{is} from the isotropic to the nematic phase enabled us to calculate the retardation factors $g_{\parallel}$ and $g_{\perp}$ [9, 10] and then the "nematic potential" q according to the relations derived by Meier and Saupe [9] and Coffey et al. [13–17]. The validity of some assumptions of the mean-field theories of the nematic state is discussed.

Experimental

The 5PCH sample was obtained from R. Dąbrowski, Military Technical University, Warsaw. Its transition temperatures agree very well with the literature data.

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In the TDS measurement the thin cell end capacitance method was used as previously described [4]. From the Fourier transform of a step pulse reflected from the empty cell, $R_1(\omega)$, and from the dielectric filled cell, $R_r(\omega)$, the ratio $\varrho_r = (R_1 - R_r)/(R_1 + R_r)$ is obtained. The complex permittivity ε_r^* is then calculated from the bilinear relation

$$\varepsilon_r^* = \varepsilon_r' - i\,\varepsilon_r'' = \frac{1 + A\,\varrho_r}{1 - B\,\varrho_r}, \quad (\mathrm{r} = \mathrm{is}, \|, \perp). \tag{1}$$

The coefficients $A = A' + iA''$ and $B = B' + iB''$, which depend on the cell dimensions and the line characteristics, can be determined by using two standard liquids of known dielectric properties.

An orienting DC field of 3000 V/cm was applied to obtain the parallel orientation in the nematic phase. For this orientation a time window 100 ns was used, and A and B were determined from calibration with chlorobenzene and acetone as standard liquids.

The perpendicular orientation was obtained by applying a magnetic field of about 0.5 T on the capacitance cell in parallel with the electrodes. For these measurements a time window of 10 ns was used, and the coefficients A and B were determined with heptane and 3-bromopentane as reference liquids. The cell dimensions were found to correspond to those of a cylindrical capacitance cell of effective length 9 mm.

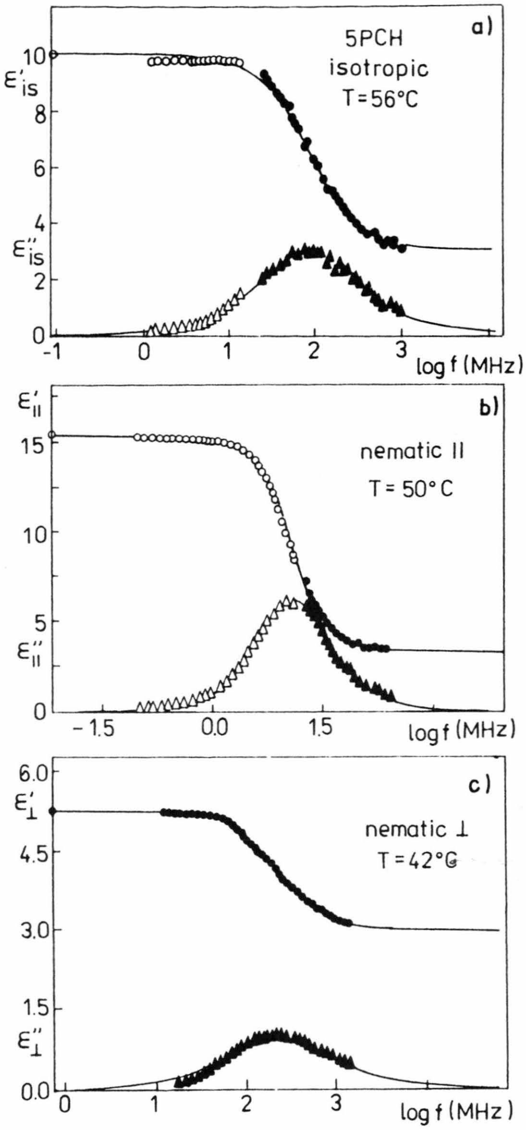

Fig. 1. Dispersion and absorption spectra for the isotropic (*a*) and two orientations of the nematic phase (*b*, *c*) of 5PCH. The open points were obtained by measurements in the frequency domain [6], filled points by the TDS method. The lines correspond to the Cole-Cole equation fitted to the points.

Results

Figures 1 and 2 show the obtained complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\,\varepsilon''$, in the isotropic (*a*) and in the nematic (*b* and *c*) phase of 5PCH. They are presented in the form of dispersion and absorption spectra (Fig. 1) and Cole-Cole diagrams (Figure 2). The opened points were obtained at the Ruhr University Bochum in the frequency domain (100 kHz – 13 MHz) [6], whereas the filled points come from the TDS spectra (the ranges of frequency are indicated in Figure 2). The consistency of the spectra measured by the two experimental methods is satisfactory (due to the cylindrical geometry of the capacitor the perpendicular component could not be measured at Bochum). The solid lines are the best fits of the Cole-Cole equation

$$\frac{\varepsilon_r^* - \varepsilon_{\infty r}}{\varepsilon_{sr} - \varepsilon_{\infty r}} = \frac{1}{1 + (i\,\tau_r\,\omega)^{1-\alpha_r}} \tag{2}$$

to the experimental points. The static permittivity ε_s was measured at 100 kHz. The parallel component of the permittivity, $\varepsilon_{\|}^*$, was well described by a simply Debye equation with $\alpha_{\|} = 0$, whereas for $\varepsilon_{\perp}^*$ and ε_{is}^* the values of α_r were about $0.10 \div 0.13$. According to the results of the studies of 7PCH presented in [3] we also used the Davidson-Cole equation to fit the spectra of the isotropic phase of 5PCH. However, contrary to the spectra of 7PCH, we did not find any indication

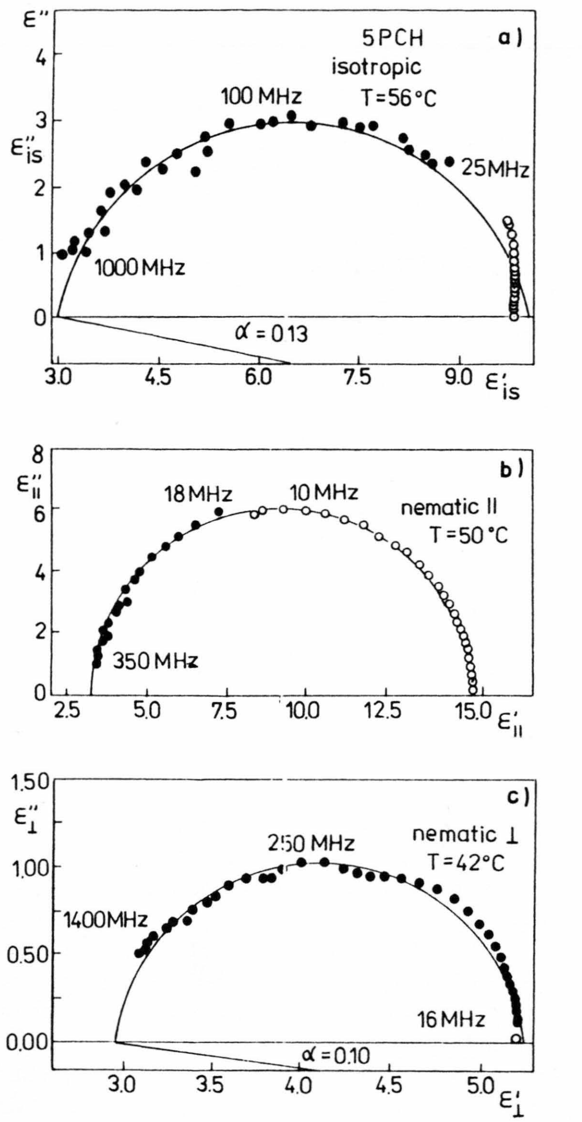

Fig. 2. The spectra from Fig. 1 presented in the form of Cole-Cole diagrams.

Table 1. Parameters of the Arrhenius equation for the relaxation processes occurring in the nematic and isotropic phases of 5PCH

Phase	Nematic, $\boldsymbol{E} \parallel \boldsymbol{n}$	Nematic, $\boldsymbol{E} \perp \boldsymbol{n}$	Isotropic
τ_a [s]	$1.15 \cdot 10^{-19}$	–	$8.8 \cdot 10^{-15}$
ΔH [kJ/mol]	69 ± 2	2 ± 2	33 ± 2

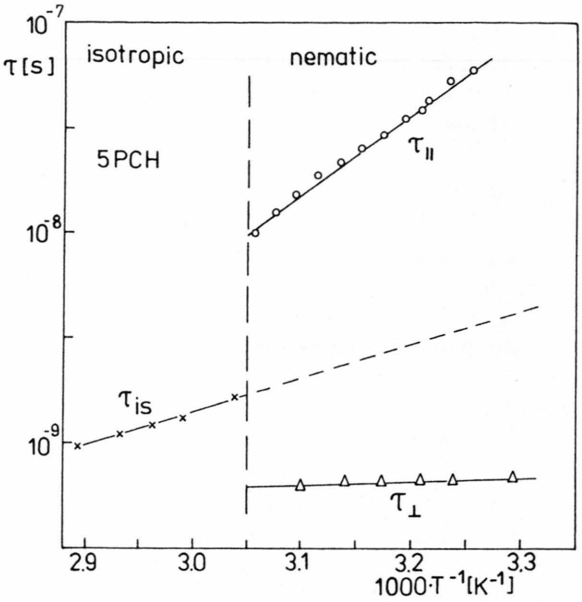

Fig. 3. Relaxation times characterizing the molecular reorientations in the isotropic and nematic phases of 5PCH versus reciprocal temperature.

supporting the assumption of a non-symmetrical distribution of the relaxation times τ_{is} in the present substance.

Figure 3 presents the dielectric relaxation times characterizing the molecular reorientations in both phases. Using the Arrhenius equation, $\tau = \tau_a \exp(\Delta H/RT)$, the activation enthalpies ΔH were calculated and given in Table 1.

Discussion

Dielectric properties of the nematic phase can be considered in the mean-field approximation [1, 9–17]. It is assumed that a rod-like molecule is under influence of a potential energy

$$U(\cos\theta) = -\,q P_2(\cos\theta)\,, \tag{3}$$

where $P_2(\cos\theta)$ is the second Legendre polynomial and θ the angle between the molecular symmetry axis and the nematic director. The nematic potential q is supposed to be related to the order parameter $S = \langle P_2(\cos\theta)\rangle$:

$$q = \mathscr{C} S\,, \tag{4}$$

where the parameter $\mathscr{C}$ depends on the molar volume.

Assuming a cosine form of the distribution function describing the orientation of the molecular symmetry axis in the nematic phase, Meier and Saupe [9] derived the formula

$$g_{\parallel} = \frac{\tau_{\parallel}}{\tau_0} = \frac{e^{\sigma}-1}{\sigma}, \tag{5}$$

where $g_{\parallel}$ is called the retardation factor, $\tau_{\parallel}$ is the relaxation time for the l.f. process, and τ_0 is the relaxation time for the same process in the absence of the nematic potential and is estimated by an extrapolation $\tau_{\text{is}}(T)$ from the isotropic to the nematic phase. Thus, dielectric relaxation studies can give some information about the nematic potential barrier parameter $\sigma = q/RT$ [1, 6, 9, 10, 18, 22–24] provided the dipole moment of the molecule is directed along the symmetry axis. In the case of 5PCH the dipole moment deviates only slightly from this axis (by ca. 18° [19]).

Recently Coffey et al. [13–17] have developed a new approach to the problem of Brownian rotational motion of a single axis rotator in a uniaxial potential. Using very sophisticated mathematical procedures they were able to obtain exact analytic solutions for the retardation factors $g_{\parallel}$ and $g_{\perp}$ $(=\tau_{\perp}/\tau_0)$ in terms of σ; the $g_{\parallel}(\sigma)$ function obtained in that way differs considerably from that predicted by (5) [17]:

$$g_{\parallel} = \frac{e^{\sigma}-1}{\sigma}\left(\frac{2}{1+1/\sigma}\sqrt{\sigma/\pi}+2^{-\sigma}\right)^{-1} \tag{6}$$

(see also Figure 4). Coffey and Kalmykov [12] have found relations between the retardation factors $g_{\parallel}$ and $g_{\perp}$ and the order parameter S:

$$g_{\parallel}^{S} = \frac{2S+1}{1-S}, \tag{7}$$

$$g_{\perp}^{S} = \frac{2-2S}{2+S}. \tag{8}$$

We believe that results of our dielectric relaxation studies of 5PCH are a good basis for a discussion of the above relations.

Using the experimental data on the longitudinal $\tau_{\parallel}$ and transverse $\tau_{\perp}$ relaxation times and approximating τ_0 by extrapolation of τ_{is} to the nematic phase as shown in Fig. 3, we calculated the retardation factors $g_{\parallel}$ and $g_{\perp}$ as functions of temperature within the nematic phase of 5PCH (Figure 5a). It turns out that the nematic ordering strongly slows down the molecular reorientations around the short axes, whereas it facilitates reorientations around the long axes. Such behaviour of both movements is predicted by the mean-field theories [10, 13–17] and can be deduced from Fig. 4 (note that $\sigma \sim q/T \sim S/T$). This corresponds also with a very high activation barrier for the l.f. process and a negligible activation barrier for the h.f. process (see Table 1). It is necessary to point out, however, that the spectra measured for perpendicular orientation of the nematic phase are rather broad (see Figs. 1c and 2c), indicating a contribution from other molecular processes (e.g. a precession of the symmetry axis around the director [21]).

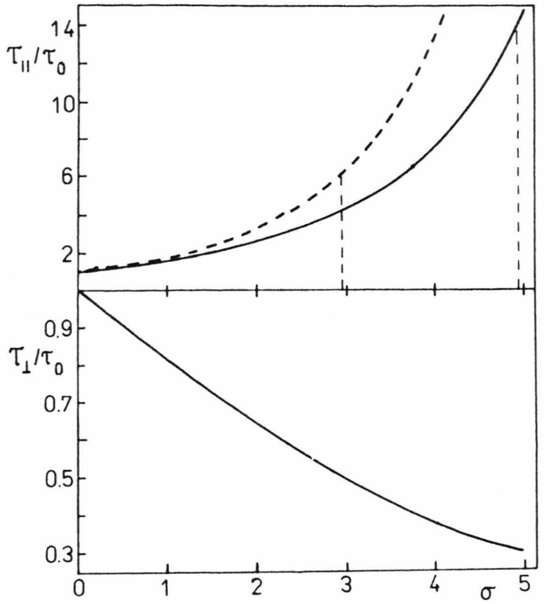

Fig. 4. Longitudinal $g_{\parallel}$ and transverse $g_{\perp}$ retardation factors as functions of the nematic potential barrier parameter σ according to Coffey et al. [13–15]. The dashed line corresponds to the Meier-Saupe formula (5). The vertical dashed lines show the range of σ considered in the paper.

Figure 5b shows that the relations between the experimental retardation factors and the order parameter S, taken from [20], are not properly described by (7) and (8): $g_{\parallel}^{S}$ is approximately two times smaller than $g_{\parallel}$, whereas $g_{\perp}/g_{\perp}^{S} \approx 0.7$ within the nematic phase of 5PCH. In the case of the parallel component, (7), agreement with the experimental retardation factor cannot be expected as the use of the effective eigenvalue method does not provide a good mathematical approximation to $g_{\parallel}$ for σ greater than 2 because of the exponential nature of that quantity [17]. However, the perpendicular component, (8), provides a close approximation to $\tau_{\perp}$ [13–17]. It is interesting to note

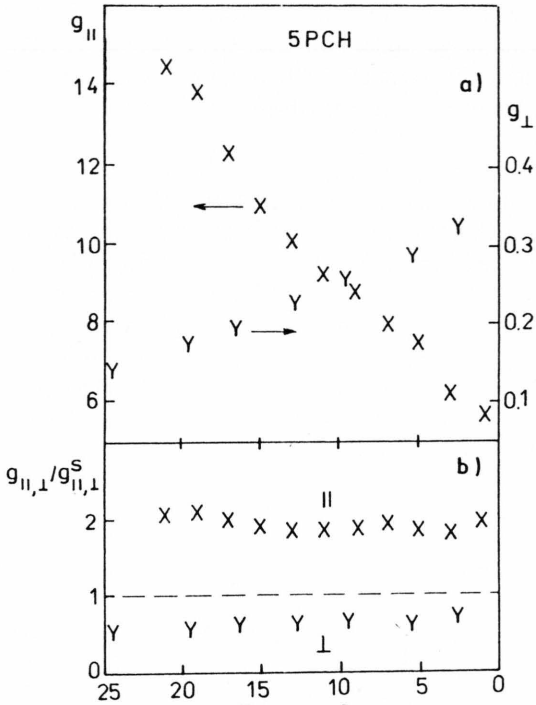

Fig. 5. (*a*) The retardation factors $g_{\parallel}$ and $g_{\perp}$ calculated from the data of Fig. 3 versus temperature within the nematic phase of 5PCH. (*b*) Ratios of the experimental retardation factors $g_{\parallel,\perp}$ to the $g^S_{\parallel,\perp}$-factors predicted by (6) and (7).

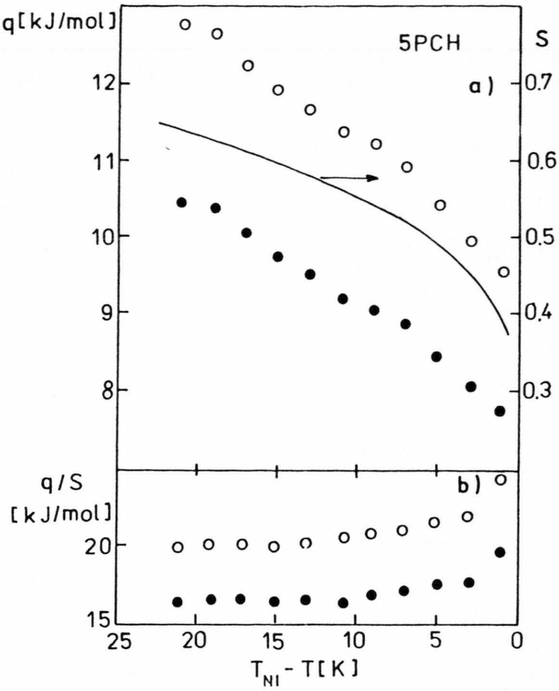

Fig. 6. (*a*) The nematic potential q and the order parameter S (solid line) [18], and (*b*) the ratio q/S versus temperature within the nematic phase of 5PCH. The filled points were obtained from the Meier-Saupe relation [9], the open points correspond to the Coffey et al. [13–15] relation (compare Figure 4).

that by combining (7) and (8) one gets $(g_{\parallel}+1)\,g_{\perp}=2$, whereas the experimental retardation factors give $(g_{\parallel}+1)\,g_{\perp}=2.5\pm0.1$ within the nematic phase of 5PCH.

There are at least two reasons that may lead to these disagreements. Firstly, this may result from the order parameter values accepted. It should be noted that the order parameter $S(T)$ values come from the refractive index data and were calculated with some model approximations (actually the Neugebauer model was used). Nevertheless, other accessible data on $S(T)$ [20, 29, 31] change both relations only slightly ($g_{\parallel}/g^S_{\parallel}\sim1.9\div2.1$, $g_{\perp}/g^S_{\perp}\sim0.65\div0.75$). Therefore the second reason may be more important. The 5PCH molecule has not, in practice, a perpendicular component of the dipole moment, and therefore the measured relaxation time $\tau_{\perp}$ cannot properly characterize the molecular rotation around the long axis in the nematic pahse. Thus, further dielectric investigations of substances having both parallel and perpendicular permanent dipole moments are required. We have undertaken such studies for *n*-alkyloxy-cyanobiphenyl (nOCB) compounds.

The value of $g_{\parallel}$ extrapolated to T_{NI} is ~5.5; so it is bigger than 4 predicted by the Maier-Saupe theory [11], or than about 3 as can be deduced from (6) (assuming $S\cong0.35$ at T_{NI} [20, 31]). It is also markedly larger than the corresponding values obtained for cyanobiphenyl (nCB) compounds (usually less than 3) [6, 18, 22–24]. Also the activation barrier for the l.f. relaxation process is higher in 5PCH than in 5CB (70 and 63 kJ/mol, respectively). This agrees with the observation that the molecules are more closely packed in the nematic phase of 5PCH than in case of 5CB [25]. All those factors, together with the change of the activation parameters with increase of pressure, observed for both compounds [6], seem to suggest stronger dipole-dipole associations in the nematic phase of 5PCH. Such associations were postulated on the basis of X-ray studies [26] and model calculations [27, 28].

Figure 6a presents the temperature dependence of the order parameter S taken from [20] and the nematic potential q calculated with use of (5) (filled points) and according to the exact formula, (6), derived by Coffey et al. [13–17] (open points) – compare Figure 4. The latter q values are systematically bigger than those predicted by the Meier-Saupe theory. One can notice from that comparison that the nematic potential is roughly proportional to the order parameter: the ratio of both quantities (note that they were obtained in independent experiments), $\mathscr{C}=q/S$, is nearly constant within the nematic phase and equals to ca. 16 or 20 kJ/mol, depending on the formula used – see Figure 6b. Thus, one of the essential assumptions of the mean-field theories, i.e. the proportionality between q and S seems to be well fulfilled in the nematic phase of 5PCH. The same was recently observed for 5CB under isothermal, isobaric and isochoric conditions [18]. However, in the case of 5CB the $\mathscr{C}$ value was markedly lower than for 5PCH (11 and 16 kJ/mol, respectively). That also suggests stronger intermolecular interactions in the PCH compound. Recently, Wu and Wu [29] have estimated $\mathscr{C}/RT_{\mathrm{NI}}$ values for 5CB and 5PCH in a more indirect way by fitting the Osipov-Terentiev theory [30] to the rotational viscosity coefficients γ_1. The obtained values, 2.6 and 2.4 respectively, differ substantially from 4.3 (5CB) and 5.9 (5PCH) obtained with the relaxation data (the Maier-Saupe theory [11] predicts $\mathscr{C}/RT_{\mathrm{NI}} \simeq 4.5$).

In conclusion one can notice that the time domain spectroscopy method gives dielectric permittivity values which agree very well with the spectra measured using standard frequency analyzers. Simultaneous analysis of the results of both types of dielectric experiments gives a good basis for the study of molecular motions in the nematic as well as in the isotropic phase of an LC substance. In th case of 5PCH we were able to test some predictions of the mean-field theories of the nematic phase.

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