Dielectric Properties of 4-methoxy-4'-cyanobiphenyl (1 OCB) in the Supercooled Isotropic and Nematic Phases

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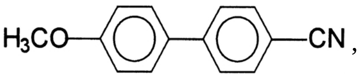
Dielectric studies of 4-methoxy-4'-cyanobiphenyl (1 OCB) in the supercooled isotropic and nematic phases were performed with the aid of three set-ups covering the frequency range 10 kHz – 5 GHz. In the static measurements the nematic phase could be supercooled down to 25 K below the clearing point, whereas in the dynamic studies a 12 K range was covered in a single run. The relaxation times and activation enthalpies characterising the molecular rotations around the principal inertia moment axes were determined. The predictions of theories based on the assumption of the rod-like molecules are well applicable to the dielectric data obtained.

Key words: Liquid Crystal; Nematic; Dielectric Properties; 1 OCB.

1. Introduction

4-Methoxy-4'-cyanobiphenyl (1 OCB),



melts to the isotropic (Is) phase at 103 °C, but on cooling it transforms from a supercooled isotropic to the monotropic nematic (N) phase at 86 °C. In spite of the inconvenience connected with supercooling, the substance seems to be very interesting due to the simplicity of its structure [1]. 1 OCB has a rigid core without the flexible tail common in other members of this and other homologous series. Such molecules can be approximated by rigid rods considered in many theories of the nematic state [1 – 7]. Partly deuterated 1 OCB was studied by Emsley et al. [1] by the deuterium NMR method. These authors determined the Saupe ordering matrix in the monotropic N phase and pointed out that in spite of a small biaxiality in the ordering matrix the assumption that the molecules may be treated as cylindrically symmetric may be doubtful.

The strong dipole moment directed along the principal molecular axis, connected with the CN group, and a small perpendicular dipole component due to the presence of the methoxy group, makes 1 OCB extremely interesting for testing the theories of the dielectric anisotropy and the dielectric relaxation processes in the nematic phase. Recently [8] the longitudinal relaxation times determined for the Is (τ_0) and N ($\tau_{\|}$) phases of 1 OCB were used for testing the theories linking the retardation factor $g = \tau_{\|}/\tau_0$ and the order parameter S. However, due to experimental difficulties connected with the frequent freezing of the monotropic N phase, the relaxation times $\tau_{\|}$ reported there were obtained in several attempts. In the present relaxation study we were able to sustain the parallel oriented nematic phase in a temperature range of 12 K until the sample froze. The obtained relaxation times differ slightly from those previously reported, however the conclusions derived from both experiments are practically the same.

2. Experimental

The 1 OCB sample was synthesized in the Institute of Chemistry, Military University of Technology, Warsaw. Its purity, 99.6%, was determined by thin-layer gas chromatography. Standard DSC measurements (5 K/min) revealed the melting point at 103.0 °C, whereas the transition to the N phase occurred at 85.7 °C. However, in other experiments the actual I-N transition depended on the cooling rate and changed between 86 °C and 78 °C. Therefore several analyses of the results were related to the actual T_{NI} values.

Three experimental set ups were used in the measurements of the dielectric permittivities: $\varepsilon_\parallel$, $\varepsilon_\perp$ and $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, where $\omega = 2\pi f$. The static permittivity components, $\varepsilon_\parallel$ and $\varepsilon_\perp$, were measured in Krakow with an impedance analyser HP4192A using a gold covered parallel plate capacitor (C $\sim$ 50 pF). The sample was oriented by a magnetic field of B $\sim$ 0.8 T. The relaxation spectra for the isotropic phase of 1 OCB were collected in the frequency range 10 MHz – 5 GHz with a time domain spectrometer (TDS) at Uppsala University, as was described in [9]. In this experiment the N phase could not be achieved, but the isotropic liquid was supercooled down to 78.4 °C. The low frequency relaxation (l. f.) process in the nematic (and also in the isotropic) phase was studied in Katowice with the aid of an Agilent 4219B impedance analyser that covered the frequency range 1 MHz – 1800 MHz. The nematic sample was oriented by a DC electric field of $\sim$ 100 V/cm. In all measurements several attempts with different cooling rates were necessary in order to achieve the nematic phase and then to keep it stable in a sufficient temperature interval. All the data were obtained with a permanent slow cooling of the sample because even a small increase in temperature during a stabilization process resulted in an immediate freezing of the sample.

3. Results

Figure 1 presents the static permittivity components, $\varepsilon_\parallel$ and $\varepsilon_\perp$, measured in independent runs. The clearing temperature was slightly different in the two runs (85.2 °C and 84.7 °C, respectively), and therefore the $\varepsilon_\perp$ data were shifted to the upper temperature. As in the case of other *n*OCB and *n*CB substances, the average value $\langle\varepsilon\rangle(\varepsilon_\parallel + 2\varepsilon_\perp)/3$ is smaller than the extrapolated $\varepsilon_{\mathrm{is}}$ value. The origin of this was recently discussed by Rzoska et al. [10].

The Cole-Cole plots from the TDS spectra of the isotropic phase of 1 OCB are presented in Figure 2. A superposition of two Debye-type processes was fitted to the spectra,

$$\varepsilon^* - \varepsilon_\infty = \frac{\delta_1}{1 + i\omega\tau_1} + \frac{\delta_2}{1 + i\omega\tau_2}, \qquad (1)$$

where $\delta_1 = \varepsilon_{\mathrm{s}} - \varepsilon_2$, $\delta_2 = \varepsilon_2 - \varepsilon_\infty$, are the strengths (increments) of the two relaxation processes, ε_{s} and ε_∞ are the static and high frequency permittivity, respectively. The calculated relaxation times, $\tau_{\mathrm{l.\,f.}}$ and $\tau_{\mathrm{h.\,f.}}$ are consistent in a broad temperature range (see Fig. 4). The extension of the isotropic region to the nematic phase seems to be the experimental confirmation of the theoretical prediction based on the molecular dynamics simulation [7].

Table 1. The preexponential factor τ_0 and the activation enthalpy ΔH according to the Arrhenius equation, $\tau = \tau_0 \exp(\Delta H/RT)$, in the isotropic and nematic phase of 1 OCB.

Phase	Relaxation process	τ_0 [s]	ΔH [kJ/mol]
Isotropic	Low frequency	5.51×10^{-15}	36.2 ± 2
	High frequency	6.45×10^{-14}	23.8 ± 4
Nematic	Low frequency	6.01×10^{-22}	87.6 ± 4

The results obtained with the 4219B analyser are presented in Fig. 3 as the dispersion and absorption spectra. The parallel permittivity $\varepsilon_\parallel$ is a bit smaller than that presented in Fig. 1 due to a weak orienting field applied (for higher bias fields the liquid sample did not “survive” the I – N transition). Due to limited frequency range available, the high frequency process could not be separated from the obtained spectra. The l. f. relaxation times were calculated as $\tau_{\mathrm{l.\,f.}} = 1/2\pi f_{\mathrm{m}}$, where f_m corresponds to the maximal loss $\varepsilon''_{\mathrm{m}}$. They are presented in Fig. 4 in form of an Arrhenius plot. Very nice concordance of the τ_{Is} values coming from the measurements in the frequency and time domains can be noted. The activation enthalpy, ΔH, calculated for particular relaxation processes according to the Arrhenius equation, are presented in Table 1.

4. Discussion

The dipole moment μ of the 1 OCB molecule can be calculated taking into account the dipole moments of both moieties: the cyano-phenyl (4.0 D [11]) and methoxy-phenyl (1.28 D, that forms an angle 72° with the *para*-axis [12]). This gives μ_{l} = 4.39 D and μ_{t} = 1.22 D for the longitudinal and transverse components, respectively, with an $\beta \approx 15.5^\circ$ between μ and the *para*-axis. On the other hand, from the experimental increments in the isotropic phase (Fig. 2) and the Onsager equation [13] one has $\delta_{\mathrm{t}}/\delta_1 \sim (\mu_{\mathrm{t}}/\mu_{\mathrm{l}})^2$ = $\mathrm{tg}^2\beta$. The estimated angle $\beta \approx 22^\circ$ is larger than the above value. However, regarding the model and experimental limitations one may conclude that the separation procedure applied for the spectra of the isotropic phase of 1 OCB yields correct data on the relaxation times characterising the molecular rotations around the principal inertia axes. Also, the spectra of the nematic phase of 1 OCB show a deviation from the Debye curves at frequencies above c. 600 MHz, but the limited range of

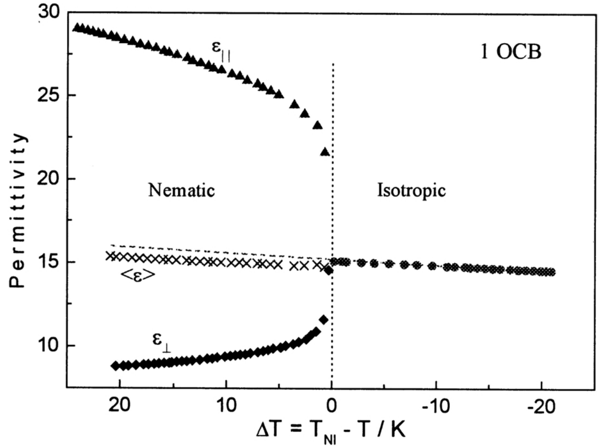


Fig. 1. Static dielectric permittivities versus reduced temperature for the isotropic and nematic phase of 1 OCB. The parallel and perpendicular components were measured in independent runs with slightly different cooling rates. The Is-N transition temperature was different in both cases.

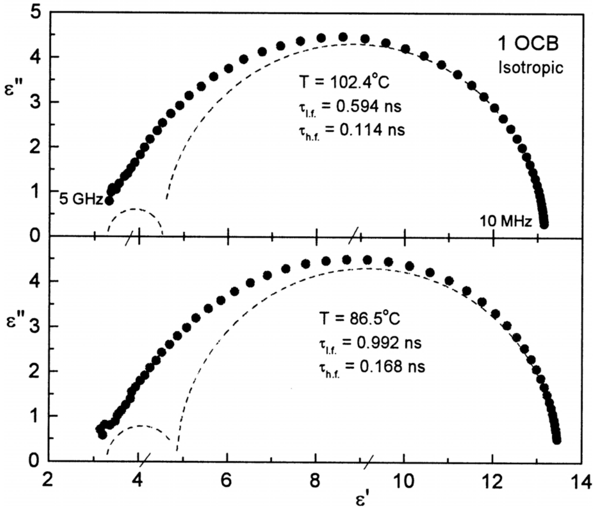


Fig. 2. Cole-Cole plots from the TDS spectra in the isotropic phase of 1 OCB. The separation of the relaxation spectra into two processes, the low frequency $\tau_{\mathrm{l.f.}}$ and high frequency $\tau_{\mathrm{h.f.}}$, was done according to (1).

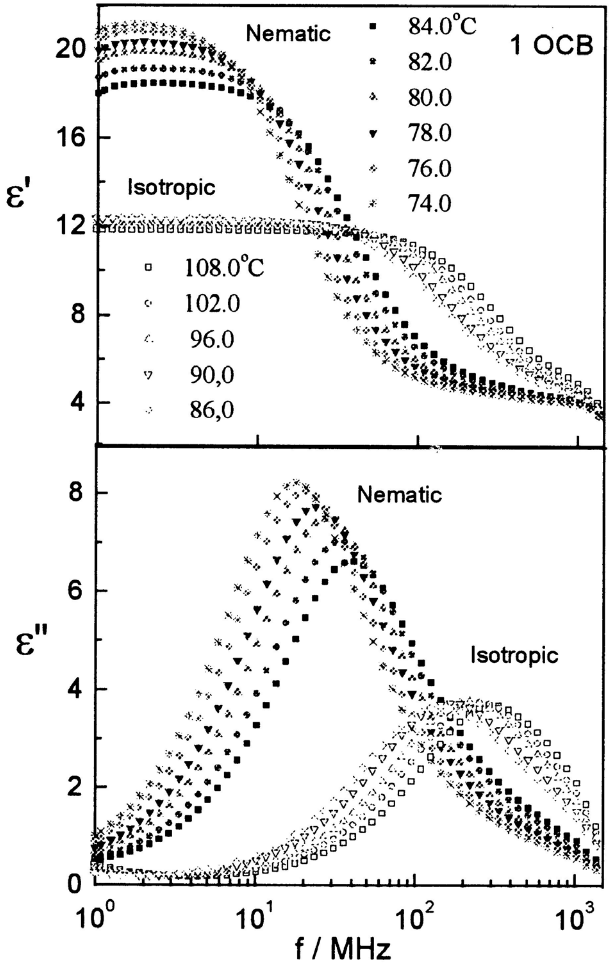


Fig. 3. Dispersion and absorption spectra in the isotropic and nematic phases of 1 OCB collected with the impedance analyzer.

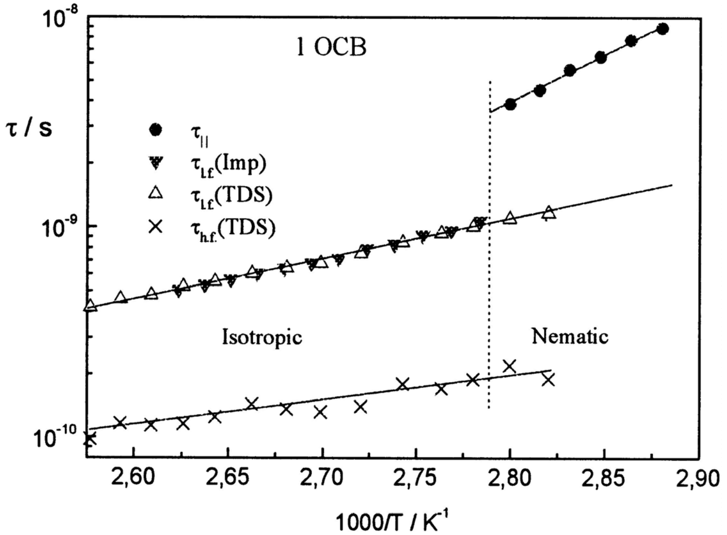


Fig. 4. Arrhenius plot from the relaxation times determined for the isotropic and nematic phases of 1 OCB.

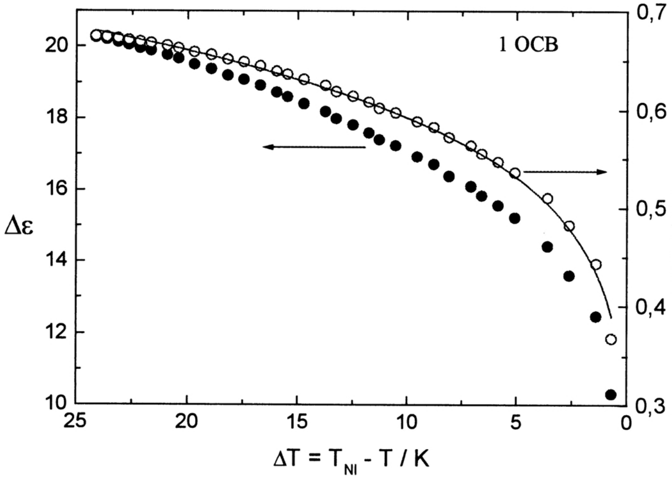


Fig. 6. The temperature dependence of the dielectric anisotropy in the nematic phase of 1 OCB (full points) and the order parameter $S \sim T \cdot \Delta\varepsilon$ resulting from the Maier and Meier theory [16]. The line is the fit of (4), yielding $\gamma = 0.157$.

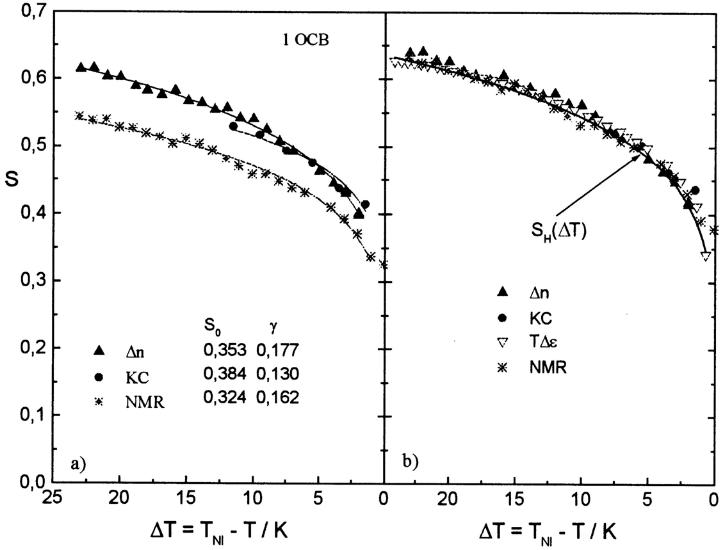


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Fig. 5. a) Order parameter for 1 OCB derived from three experiments: NMR [1], optical anisotropy Δn [8], and the Coffey et al. theory. The parameters from the fits of the Haller equation to the points are shown. b) The points from Fig. 5a and Fig. 6 ($T\Delta\varepsilon$) normalized at $\Delta T = 10$ K to the line corresponding to $S_{\mathrm{H}}(T) = (T_{\mathrm{NI}})^{-0.17}(\Delta T)^{0.17}$.

frequencies available in the impedance analyser does not allow for an extraction of the high frequency relaxation process.

In the recent papers [8,14] the low frequency relaxation times $\tau_\parallel$ and τ_0 (as extrapolated from the isotropic phase) were used for the calculation of the nematic order parameter $S = \langle P_2(\cos\theta)\rangle$, where θ is the angle between the long molecular axis and the nematic director **n**. Using the formulae derived by Coffey et al. [4–6],

$$g_\parallel = \frac{\tau_\parallel}{\tau_0} = \frac{e^\sigma - 1}{\sigma}\left(\frac{2}{1+1/\sigma}\sqrt{\sigma/\pi} + 2^{-\sigma}\right)^{-1}, \quad (2)$$

$$\sigma \approx \frac{3S(5-\pi S)}{2(1-S^2)}, \quad (3)$$

the order parameter for several different nematics was calculated and compared with those obtained with the aid of other experimental techniques. The main conclusions were as follows:

1. A large disagreement of the $S(T)$ behaviour coming from different experimental methods was noted.

2. In most cases the differences between particular sets of data were markedly larger than the experimental errors (usually ca. 5% or less).

3. The NMR measurements usually yield smaller *S*-values than the magnetic susceptibility and optical anisotropy methods.

4. The data obtained for rigid molecules by the Coffey et al. (KC) theory are fairly close to the results coming from experimental methods giving a more straightforward connection of *S* with the measured quantity.

5. The more rigid the molecule, the larger the KC-values, and thus they are closer to the values coming from optical and magnetic susceptibility measurements.

6. Most of the *S(T)* behaviour can well be approximated by the Haller [15] formula

$$S_\mathrm{H}(T) = S_0(T_\mathrm{NI} - T)^\gamma \quad (4)$$

with the two adjustable parameters S_0 and γ.

7. A scaling procedure based on the Haller formula (4) with $S_0 = (T_\mathrm{NI})^{-\gamma}$ reduces the scatter of experimental sets of points to a reasonable range; this means that the temperature variation of the order parameter, $S(T)$, is properly established in most of experiments.

The present relaxation data strongly support the above conclusions, as can be seen in Fig. 5a,b. The *S*-values calculated with the use of (3) and (4) coincide with the optical results. In the inset the fitting parameters S_0 and γ are shown. The γ-value for KC differs from the others because of the limited temperature range available in the present relaxation experiment.

In addition to the above, we may consider the dielectric anisotropy $\Delta\varepsilon$ that was established in distinctly broader temperature interval (see Fig. 1). According to the Maier and Meier theory [16], for strongly polar molecules one has $\Delta\varepsilon \sim S(T)/T$. In Fig. 6 the temperature dependence of the anisotropy itself and $S \sim T \cdot \Delta\varepsilon$ are shown. By fitting the Haller-type formula to the $T \cdot \Delta\varepsilon$ points we have γ = 0.157, which is fairly close to other γ-values. In Fig. 5b all the data are normalised at ΔT = 10 K to the line corresponding to $S_\mathrm{H}(T) = (T_\mathrm{NI})^{-0.17}(\Delta T)^{0.17}$. As in the previous analyses [8] such re-scaling of the *S(T)*-values leads to a considerable reduction of the experimental sets of points.

Finally, one may conclude that the predictions of theories based on the assumption of rod-like molecules are well applicable to the dielectric data obtained for 1 OCB.

Acknowledgements

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