

# Dielectric Relaxation in Nematic and Isotropic Phases of 4-(*trans*-4'-*n*-Propylcyclohexyl)isothiocyanatobenzene

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The results of a dielectric relaxation study (in the frequency region from about 1 kHz to 1 GHz) of the liquid crystalline title compound ( $C_3H_7$ -Cyhx-Ph-NCS, 3-CHBT) in the isotropic and the nematic phase (measurements with electric field parallel to alignment) are presented. The spectra of both phases can be described by two relaxation processes of Debye-type, possibly related to rotation around the long and short molecular axes.

## 1. Introduction

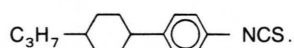
Among experimental methods which are used to study the molecular dynamics in liquid crystalline materials, dielectric relaxation spectroscopy is of special interest [1, 2] since it generally detects, over a wide frequency range, the stochastic reorientational motion of polar molecules as whole entities as well as the motion of their polar fragments. By application of a magnetic field or by an appropriate treatment of the vessel walls, a nematic sample can be ordered, and in that situation dielectric spectroscopy offers the opportunity to study molecular dynamics along certain directions with respect to the nematic director.

The appearance of the nematic potential and the increase in viscosity at the isotropic–nematic phase transition cause remarkable alterations in the dielectric spectrum. Many papers, both theoretical [3–6] and experimental [7–16] have been published on that subject.

It has been shown by Martin et al. [4] that in the presence of a nematic potential for example of the Maier-Saupe type [17] the dynamic dielectric properties are anisotropic. In the case of a probing electric field  $E$  parallel to the nematic director  $n$ , the main relaxation process, which usually is related to the end-over-end tumbling motion of the molecule and, consequently, of the dipole moment parallel to the principal molecular axis, is slowed down in comparison to the

isotropic phase, according to the diffusion over the nematic barrier. If the field  $E$  is perpendicular to  $n$ , one observes in most cases a broadened dielectric spectrum the interpretation of which is more difficult [18, 19].

In this paper we consider an example from the class of phenylcyclohexane based liquid crystals, namely 4-(*trans*-4'-*n*-propylcyclohexyl)isothiocyanatobenzene (3-CHBT):



To our knowledge, the dynamic dielectric properties of that compound have not yet been reported. We present results for the frequency dependence of the complex permittivity  $\epsilon^* = \epsilon' - i\epsilon''$  as measured in the isotropic phase, and of  $\epsilon_{\parallel}^*$  as measured *parallel* to the molecular alignment with oriented samples in the nematic phase, i.e. with the electric field  $E$  parallel to the nematic director  $n$ .

## 2. Experimental

3-CHBT was synthesized and purified in the Institute of Chemistry, Military Technical Academy, Warsaw, by the procedure described by Dąbrowski et al. [20]. The temperatures of the phase transitions were the following:

Cr 38.5°C N 41.5°C I.

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The complex permittivity was measured at seven different temperatures. Three of them (50, 45 and 43 °C) correspond to the isotropic phase and four (40, 39; supercooled: 36 and 34 °C) to the nematic phase of 3-CHBT. The measurements were carried out in the frequency region from about 1 kHz to 1 GHz with two impedance analyzers HP 4191 A and HP 4192 A connected to a HP 87 computer. The measuring cell consisted of a parallel-plate capacitor terminating a coaxial line [21, 22]. A magnetic field of 1.2 T was used to align the molecules in the nematic phase. All measurements in the nematic phase were performed for the case  $\mathbf{E} \parallel \mathbf{B}$  ( $\mathbf{E} \parallel \mathbf{n}$ ). The temperature was measured with an accuracy better than 1% and maintained constant within  $\pm 0.1$  °C. The overall accuracy was better than 2% for  $\epsilon'$  and 5% for  $\epsilon''$ .

### 3. Results and Discussion

Figures 1 and 2 present the results of the permittivity measurements for the isotropic (I) and the nematic

(N) phase of 3-CHBT. They show a considerable change of spectral features at the isotropic–nematic phase transition: The dielectric relaxation strength increases and the effective relaxation time (corresponding to the maximum of energy absorption) increases, too. For a quantitative analysis of these results, a log-log representation of the frequency dependence of the imaginary part of permittivity,  $\epsilon''(F)$ , is helpful. In Fig. 3 two plots of that kind, one for the isotropic (50 °C) and the other for the nematic phase (39 °C), are shown as examples. In any case the experimental slope of  $\log \epsilon''$  vs.  $\log F$  on the *low frequency side* equals unity within experimental error. On the *high frequency side*, however, the situation is different for both phases. In the nematic phase the appearance of a second absorption band at higher frequencies is obvious, whereas in the isotropic phase the linearity in the  $\log \epsilon''$  vs.  $\log F$  dependence, observed up to the highest frequencies employed, does not unambiguously allow for such an inference. Rather the spectrum can be described by a Cole-Davidson function [22] in that case, similar to the findings for shorter, but still elongated molecules [23].

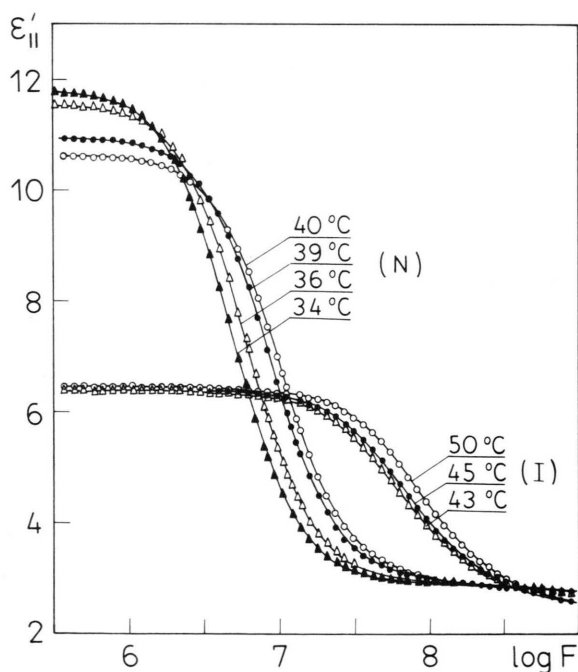


Fig. 1. Real part of the permittivity ( $\epsilon'$ ) as a function of the probing electric field frequency ( $F$ ) in isotropic (I) and nematic (N) phases of 3-CHBT. In nematic phase the permittivity was measured in the direction parallel to the molecular alignment.

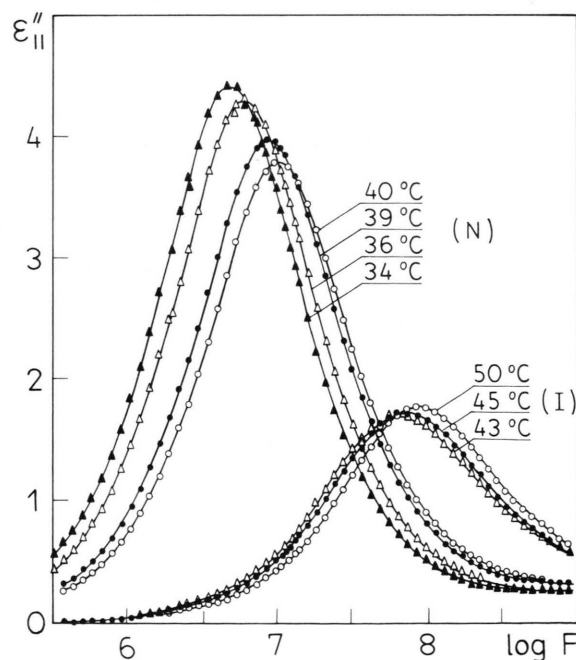


Fig. 2. Imaginary part of the electric permittivity ( $\epsilon''$ ) as a function of the frequency ( $F$ ) in isotropic (I) and nematic (N) phases of 3-CHBT. In nematic phase the permittivity was measured in the direction parallel to the molecular alignment.

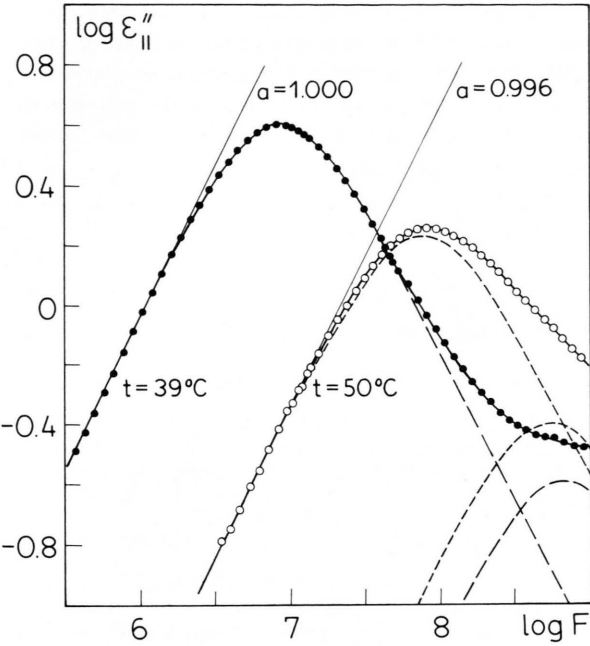


Fig. 3. Frequency dependence of the  $\varepsilon''$  in the isotropic (50 °C) and nematic (39 °C) phases of 3-CHBT in the double logarithmic representation. The dashed lines represent the result of the decomposition of experimental spectra into two Debye-type absorption bands.

Dielectric relaxation spectra obtained by Buka et al. [7] and by Bose et al. [8] in the frequency range up to 10 GHz for the nematic as well as the isotropic phases of alkyl( $C_n$ )cyanobiphenyls ( $n$ -CB) were interpreted as a sum of two relaxation contributions of Debye-type. Our data for  $n$ -TPEB's,  $C_nH_{2n+1}-\phi-\phi-CH_2CH_2-\phi-NCS$ , that means for molecules which are longer than 3-CHBT or  $n$ -CB, show without any doubt that the dielectric spectra for the isotropic phase consist of two absorption bands [25]. Those comparative results suggest to separate the present spectra for the isotropic phase into two Debye-type components, too.

In Fig. 3 the dashed lines represent the decomposition of experimental spectra into two Debye-type bands,

$$\varepsilon'(\omega) = \varepsilon_\infty + \sum_{i=1}^2 A_i \frac{1}{1 + \tau_i^2 \omega^2};$$
$$\varepsilon''(\omega) = \sum_{i=1}^2 A_i \frac{\tau_i \omega}{1 + \tau_i^2 \omega^2},$$

where  $A_i$  and  $\tau_i$  denote the dielectric relaxation strength and relaxation time, respectively. These quantities are

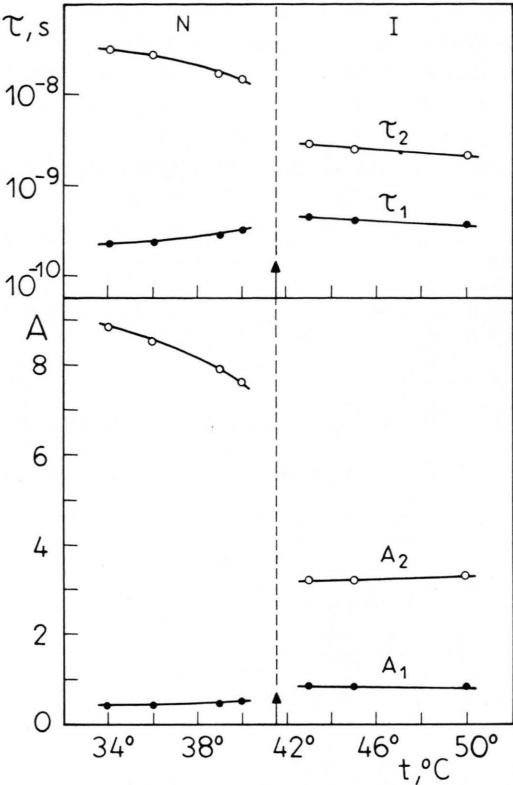


Fig. 4. Relaxation times ( $\tau$ ) and strengths ( $A$ ) as a function of temperature in isotropic ( $I$ ) and nematic ( $N$ ) phases of 3-CHBT.

Table 1. Values of the dielectric relaxation parameters: dielectric strengths ( $A_i$ ) and relaxation times ( $\tau_i$ ) for isotropic ( $I$ ) and nematic ( $N$ ) phases of 3-CHBT.

|     | $t, ^\circ C$ | $A_1$ | $\tau_1 \times 10^{10} s$ | $A_2$ | $\tau_2 \times 10^8 s$ |
|-----|---------------|-------|---------------------------|-------|------------------------|
| $I$ | 50°           | 0.808 | 3.59                      | 3.309 | 0.208                  |
|     | 45°           | 0.838 | 4.00                      | 3.240 | 0.256                  |
|     | 43°           | 0.862 | 4.37                      | 3.182 | 0.283                  |
| $N$ | 40°           | 0.501 | 3.03                      | 7.587 | 1.56                   |
|     | 39°           | 0.476 | 2.73                      | 7.936 | 1.81                   |
|     | 36°           | 0.448 | 2.36                      | 8.562 | 2.62                   |
|     | 34°           | 0.416 | 2.23                      | 8.836 | 3.25                   |

adjustable parameters in the fitting procedure. The values of  $A_i$  and  $\tau_i$  obtained for each temperature are given in Table 1, and plots of these parameters against temperature are presented in Figure 4.

It may be noticed that significant changes at the isotropic–nematic phase transition are found only for  $A_2$  and  $\tau_2$ . The increase in the relaxation time is nearly

one order of magnitude. As for other nematogens, this main dielectric relaxation process is probably related to the molecular rotation around the short axis, which is strongly influenced by the nematic potential. The high frequency absorption band ( $A_1$ ,  $\tau_1$ ) corresponds to a kind of motion which is only slightly influenced

by the presence of nematic potential. This may be a rotation around the long axis, provided that a normal component of the dipole moment occurs, or small angle fluctuation of the direction of the dipole moment. Both processes are conceivable in view of the flexibility of the molecule.

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