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Dielectric and viscous properties of 6CHBT in the isotropic and nematic phases

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This paper presents the results of measurements of the principal electric permittivities $\varepsilon_{\parallel}^*(T, \omega)$ and $\varepsilon_{\perp}^*(T, \omega)$ and the viscosity for 4-(*trans*-4-*n*-hexylcyclohexyl)isothiocyanatobenzene (C_6H_{13}–CyHx–Bz–N=C=S, 6CHBT). In the nematic phase, the Miȩsowicz η_2 viscosity coefficient was measured in a sample oriented due to the flow. On the basis of the temperature dependence of the static permittivities, using the Maier–Meier equations, the angle β between the dipole moment vector and the long axis of the 6CHBT molecule, the square of the molecular apparent dipole moment μ_{app}^2 and the nematic order parameter $S(T)$, were determined. From the temperature dependence of the viscosity and the relaxation time corresponding to the molecular rotation around the short axis, the strength of the nematic potential and the effective length of the 6CHBT molecule (in the isotropic phase) were estimated.

1. Introduction

In our recent papers, new approaches to the molecular interpretation of the static [1] and dynamic [2] dielectric properties of nematic liquid crystals, have been proposed. The temperature and the frequency dependences of the principal electric permittivities measured, respectively, parallel $\varepsilon_{\parallel}^*(T, \omega)$ and perpendicular $\varepsilon_{\perp}^*(T, \omega)$ to the molecular alignment (director **n**), can provide molecular data which are not accessible from investigations of non-oriented/isotropic liquids.

One of the most important molecular quantities which results from the analysis of the static permittivities $\varepsilon_{\parallel}^*(T)$ and $\varepsilon_{\perp}^*(T)$ is the value of the angle between the resultant dipole moment of the nematogen molecule and its long axis. There are no other experimental methods which allow one to obtain this quantity for a molecule existing in the liquid state. Studies of the dielectric relaxation in oriented nematics can give important molecular data provided that the viscosity of the system is known. Being aware of the approximation which is made in the identification of the microscopic and bulk viscosities, from the temperature dependences of the dielectric relaxation time (corresponding to the molecular rotation around the short axis) and the viscosity, one can estimate the strength of the nematic potential [3]. In the isotropic phase the relation between the relaxation time and the viscosity at different temperatures, allows one to estimate the size of the cavity corresponding to the rotating mesogenic molecule [4].

2. Experimental

2.1. *Materials*

The nematic liquid crystal 6CHBT has the following sequence of phase transitions: Cr 12.7° N 43.1° I. It was synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw.

2.2. *Characterization*

The static electric permittivity was measured with a Wayne Kerr 6425 precision component analyser at 10 kHz: the frequency is low enough to ensure the static dielectric behaviour of the 6CHBT and high enough to avoid effects due to ionic conductivity of the sample. The dielectric relaxation was measured with HP 4191A

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and HP 4192A impedance analysers in the frequency range 100 kHz–1 GHz. The nematic samples were placed in the plane capacitor and oriented with a magnetic field **B** of about 1 T. The accuracy of the measurements of the static and dynamic permittivities was 0.05% and 0.1%, respectively.

The viscosity was measured with a Haake viscometer Rotovisco RV20 with the measuring system CV 100, the shear rate being 140 s^{-1}. The measuring system consisted of the rotary beaker filled with the liquid being studied and the cylindrical sensor of the Mooney–Evart type (ME15), placed in the centre of the beaker; the liquid gap was 0.5 mm.

Density measurements were carried out with an Anton Paar DMA 60/602 vibration tube densimeter with an accuracy of 5×10^{-5} g cm^{-3}.

3. Results and discussion

3.1. *Static permittivities*

Figure 1 (*a*) presents the temperature dependence of the static permittivities measured for the nematic and isotropic phases of 6CHBT. The results can be interpreted with the use of the Maier–Meier equations [5]:

$$\varepsilon_{\parallel}(T) = 1 + \frac{NhF}{\varepsilon_0}\left\{\bar{\alpha} + \frac{2}{3}\Delta\alpha S + F\frac{\mu_{\mathrm{app}}^2}{3kT}\left[1 - (1 - 3\cos^2\beta)S\right]\right\} \qquad (1)$$

$$\varepsilon_{\perp}(T) = 1 + \frac{NhF}{\varepsilon_0}\left\{\bar{\alpha} - \frac{1}{3}\Delta\alpha S + F\frac{\mu_{\mathrm{app}}^2}{3kT}\left[1 + \frac{1}{2}(1 - 3\cos^2\beta)S\right]\right\} \qquad (2)$$

where $\varepsilon_0 = 8.85$ pF m^{-1}, N is the number of molecules per unit volume, and h and F are the Onsager local field factors [6]. The $\bar{\alpha}$ and $\Delta\alpha$ are the mean value and the anisotropy of the polarizability, respectively.

There are three unknown quantities in equations (1) and (2). Two of them concern the nematogen molecule and they are: (i) the angle β between the total dipole moment μ of the molecule and its long axis; (ii) the square of the apparent dipole moment μ_{app}^2 of the molecule; (iii) the (macroscopic) nematic order parameter $S(T)$.

In a 'normal' procedure for the fitting of the Maier–Meier equations to the experimental data, the $S(T)$ dependence is taken from another experiment, for example from the optical or magnetic anisotropy measurements. However, as shown in [1], the values of β and $\mu_{\mathrm{app}}^2(T)$ resulting from the fitting are very sensitive to the $S(T)$ function and even the change of a few % in $S(T)$ (typical for differences in $S(T)$ determined by different methods) gives significant changes in β and μ_{app}^2. It is not an exceptional case when fitting leads to a non-physical result: the different $\mu_{\mathrm{app}}^2(T)$ dependences must be taken in equations (1) and (2) to reproduce the experimental data $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$, respectively. Such a result is often interpreted as an anisotropy in the dipole–dipole interactions, disregarding the fact that the $\mu_{\mathrm{app}}^2(T)$ function in both Maier–Meier equations (1) and (2) is by definition the same. So, the fitting procedure must include the following additional condition: at a given temperature the value of μ_{app}^2 in equations (1) and (2) must be the same. That obvious condition makes the fitting of the Maier–Meier equations to the experimental data unequivocal and, as a result, one obtains the values of the three quantities: β, $\mu_{\mathrm{app}}^2(T)$ and $S(T)$ [1].

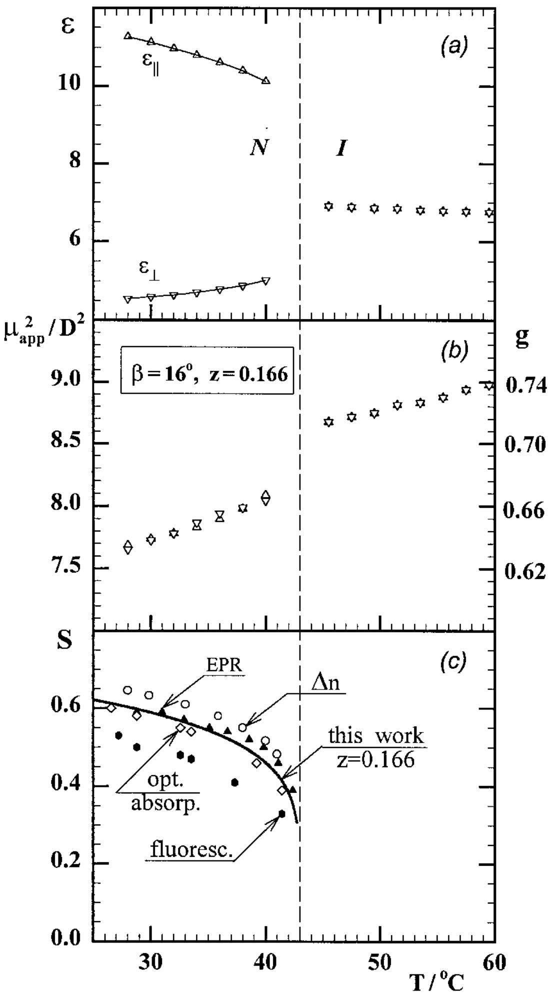

Figure 1. The solid lines in (*a*) are the best fitting of the Maier–Meier equations (1) and (2) to the experimental values of the static permittivities (points) of 6CHBT for $\beta = 16°$ and $z = 0.166$ (*b*). In (*c*) the $S(T)$ dependence obtained is compared with that resulting from the measurements of the optical Δn [8], EPR [9], optical absorption [10] and fluorescence [10] anisotropies.

The fitting procedure is much simplified when the $S(T)$ dependence is expressed in an empirical formula [7]:

$$S(T)=\left(1-\frac{T}{T_{\mathrm{NI}}}\right)^{z} \qquad (3)$$

where T_{NI} denotes the nematic to isotropic phase transition temperature (in K). The temperature dependence of the nematic order parameter is then determined by one parameter (z) only.

The values of $\bar{\alpha}=38.2\times10^{-24}\,\mathrm{cm}^3$ and $\Delta\alpha=12.2\times10^{-24}\,\mathrm{cm}^3$ for 6CHBT were taken from [8].

The solid lines in figure 1 (*a*) represent the best fitting of the Maier–Meier equations (1) and (2) to the measured permittivities. The condition concerning μ^2_{app} in the nematic phase is fulfilled, as can be seen in figure 1 (*b*). The figure also displays the value of β and z resulting from the fitting. The solid line in figure 1 (*c*) represents the $S(T)$ function plotted for $z=0.166$. The $S(T)$ dependence obtained is very close to that resulting from studies of the anisotropy of optical absorption of 6CHBT doped with some dyes [10].

In figure 1 (*b*) the values of the $\mu^2_{\mathrm{app}}(T)$ are expressed in the dimensionless quantity $g=\mu^2_{\mathrm{app}}/\mu^2_1$, where μ_1 denotes the dipole moment of a single 6CHBT molecule ($\mu_1=3.5$ D [11]). Values of g less than unity show the occurrence of antiparallel dipolar correlations. The transition from the isotropic phase to the nematic phase manifests itself by an essential increase in the degree of dipolar association (a decrease of g).

3.2. *Dielectric relaxation*

Figure 2 presents, as an example, the frequency dependences of the real (*a*) and imaginary (*b*) parts of the electric permittivities measured for the isotropic phase (at 50°C) and the nematic phase ($\varepsilon_\parallel$ and $\varepsilon_\perp$, at 34°C) of 6CHBT. In figure 2 (*c*) the results are presented in the form of Cole–Cole plots.

Studies of molecular dynamics with the dielectric relaxation method concern only those movements which are followed by changes of the projection of the molecular dipole moment on the direction of the measuring electric field vector **E**. In general, the molecular dynamics of the system studied reflects in the dielectric spectrum several simultaneously occurring movements, so that the spectrum presents a complex structure. The resolution of the spectrum into elementary absorption bands, and the attribution of the bands to particular modes of the molecular movement, are the most important problems in dielectric relaxation studies.

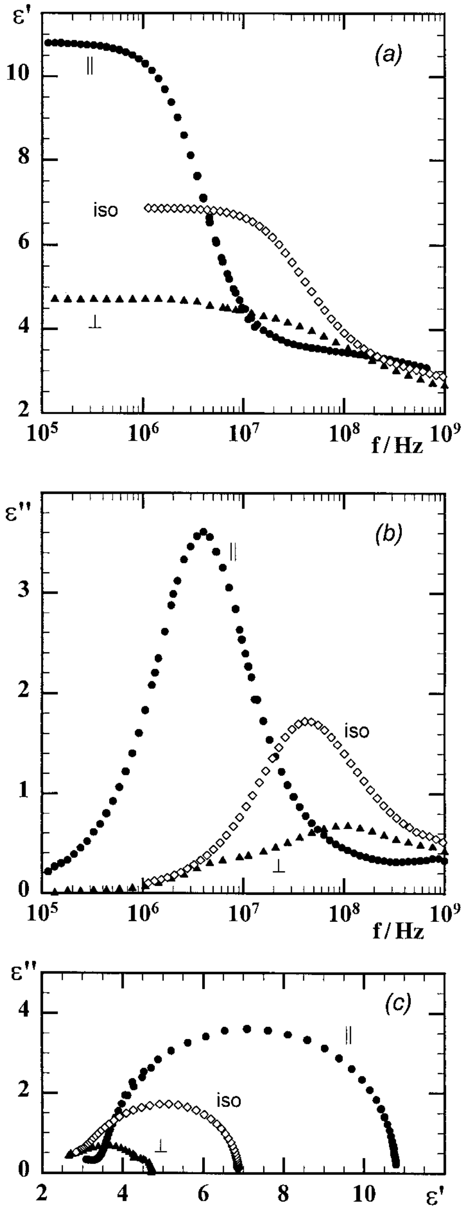

Figure 2. The frequency dependence of the real (*a*) and imaginary (*b*) parts of the principal electric permittivities measured in the oriented (**E**∥ **n** and **E**⊥**n**) nematic phase (at 34°C) and in the isotropic phase (at 50°C) for 6CHBT. In (*c*) the results are presented in the form of Cole–Cole plots.

The dielectric relaxation spectra of 6CHBT can be analysed with the use of the recently proposed model of the dynamics of nematogenic molecules in oriented nematic samples [2]. The model is depicted in figures 3 and 4: the molecules rotate around the three axes of symmetry—two of them concern the molecule itself (the long and short molecular axes) and the third axis is the director **n**. The energy absorption due to these three modes of molecular rotation can be expected in the frequency region from about 10 MHz to several GHz.

The most essential feature of the studies of oriented nematics is that for the two principal mutual orientations

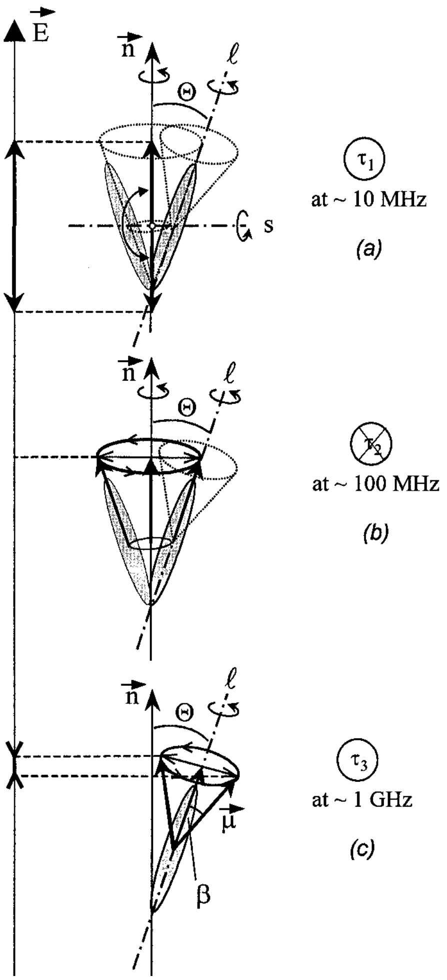

Figure 3. For a perfectly oriented nematic sample with $\mathbf{E}\parallel\mathbf{n}$, the dielectric relaxation spectrum $\varepsilon_\parallel^*(\omega)$ should be composed of two absorption bands: at ~10 MHz and at ~1 GHz.

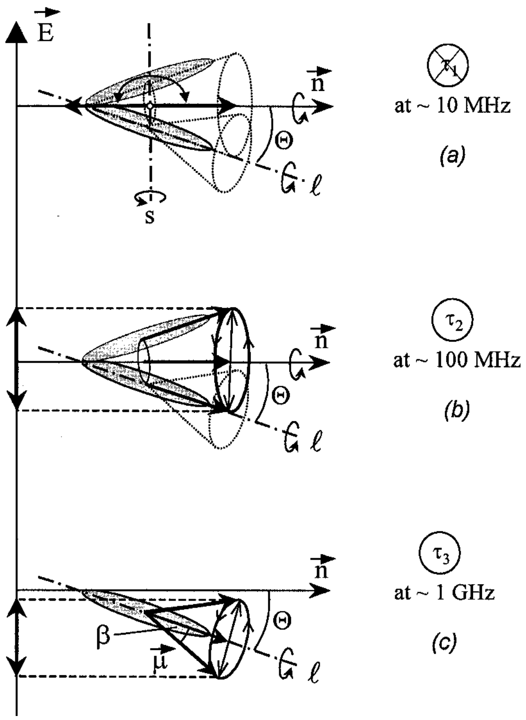

Figure 4. For a perfectly oriented nematic sample with $\mathbf{E}\perp\mathbf{n}$, the dielectric relaxation spectrum $\varepsilon_\perp^*(\omega)$ should be composed of two absorption bands: at ~100 MHz and at ~1 GHz.

of **E** and **n**, i.e. for $\mathbf{E}\parallel\mathbf{n}$ and $\mathbf{E}\perp\mathbf{n}$, one records the different spectra of the dielectric absorption, $\varepsilon_\parallel^*(\omega)$ and $\varepsilon_\perp^*(\omega)$, as they reflect the different modes of molecular motions.

It was shown in [2] that only the dielectric absorption due to rotation around the molecular long axis, which is characterized by the shortest relaxation time (τ_3), appears in both the $\varepsilon_\parallel^*(\omega)$ and $\varepsilon_\perp^*(\omega)$ spectra (as band 3) with approximately the same strengths. For perfectly oriented nematic samples, the band 1, corresponding to molecular rotation around the short axis, should appear only in the $\varepsilon_\parallel^*(\omega)$ spectrum, figure 3(*a*); the band 2, corresponding to molecular rotation on the cone around the director **n** should appear only in the $\varepsilon_\perp^*(\omega)$ spectrum, figure 4(*b*).

The model presented in figures 3 and 4, and after every attempt at the molecular elucidation of nematic properties, takes the molecular long axis l as the direction of reference. It concerns both the single molecule (for example, the direction of the dipole moment vector is defined with respect to the l axis) and the macroscopic description of the ordered nematic sample (for example, the order parameter S is a function of the angle Θ between the director **n** and the l axis). The latter case can produce some misunderstandings, because the external forces used for the nematic ordering (the electric or magnetic field) align the nematogen molecules according to the axis of their maximum of the electric or magnetic polarizability, respectively. Neither of the two axes are parallel to the molecular long axis l, which corresponds to the minimum of the momentum of inertia of the molecule. For this physical reason, the experimental dielectric spectra, both $\varepsilon_\parallel^*(\omega)$ and $\varepsilon_\perp^*(\omega)$, recorded even for a nematic sample which seems to be 'perfectly' ordered, are composed of the three absorption bands. As can be seen in figures 5(*a*) and 5(*b*), this is also the case for 6CHBT that is being studied here: the band 2 was found in the $\varepsilon_\parallel^*(\omega)$ spectrum, and the band 1 in the $\varepsilon_\perp^*(\omega)$ spectrum.

The resolution of the experimental dielectric spectra into elementary contributions was performed with the

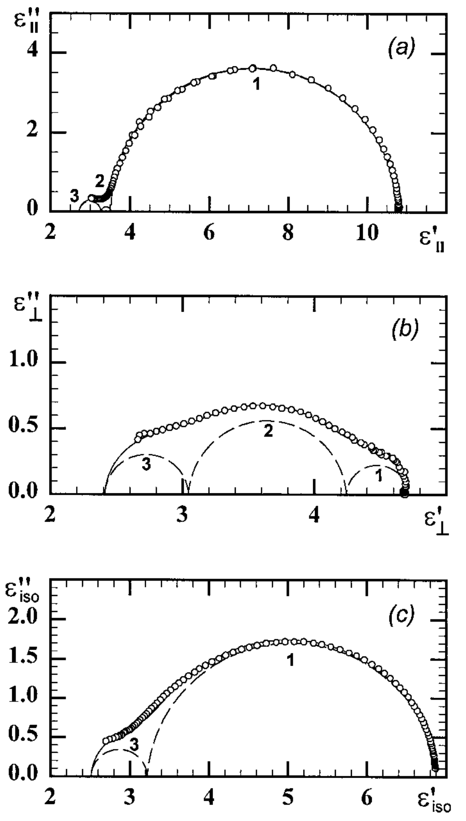

Figure 5. The dashed lines represent the elementary contributions to the total dielectric absorption corresponding to the different modes of the molecular rotations in the nematic (*a*, *b*) and isotropic (*c*) phases of 6CHBT.

use of an empirical Cole–Cole formula [12]:

$$\varepsilon_a^* = \varepsilon_a'(\omega) - \mathrm{i}\varepsilon_a''(\omega) = \varepsilon_\infty + \sum_i \frac{A_i}{1+(\mathrm{i}\omega\tau_i)^{1-k_i}} \quad (a = \parallel, \perp) \tag{4}$$

where the k_i parameter refers to the distribution of the relaxation times. For the limiting value $k_i = 0$, the i-th reorientational process is described by a single relaxation time (the Debye-type process). A_i and τ_i denote the dielectric strength and the relaxation time, respectively. A_i, τ_i and k_i are the adjustable parameters in the procedure for the fitting of equation (4) to the experimental data. The ε_∞ is the high frequency value of the permittivity.

The dashed lines in figure 5 represent the elementary spectra of dielectric absorption which correspond to the three modes of the molecular dipole reorientations shown in figures 3 and 4. As expected, the dielectric spectrum of 6CHBT in the isotropic phase, figure 5 (*c*), is composed of the two absorption bands, which correspond to the molecular rotation around the short (band 1) and long (band 3) axes.

Resulting from the fitting procedure, the values of the k_i parameters were about 10^{-2} for all elementary contributions, i.e. the contributions are very close to the Debye-type. The temperature dependences of the relaxation times τ_i and the dielectric strengths A_i are presented in figures 6 and 7, respectively.

The isotropic to nematic phase transition in 6CHBT has two spectral consequences:

(i) A new absorption band (2) appears as a result of a new mode of molecular movement arising in oriented nematics—the rotation of the molecules on the cone around the director **n**, figure 4 (*b*). This band predominates in the $\varepsilon_\perp^*(\omega)$ spectrum and appears often as a residual band in the $\varepsilon_\parallel^*(\omega)$ spectrum.

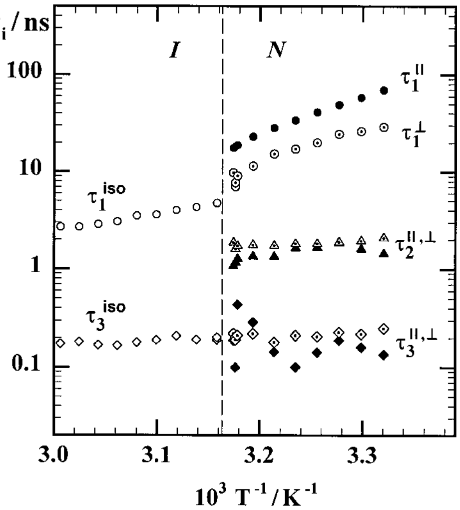

Figure 6. The temperature dependence of the relaxation times corresponding to the different modes of rotation of 6CHBT molecules.

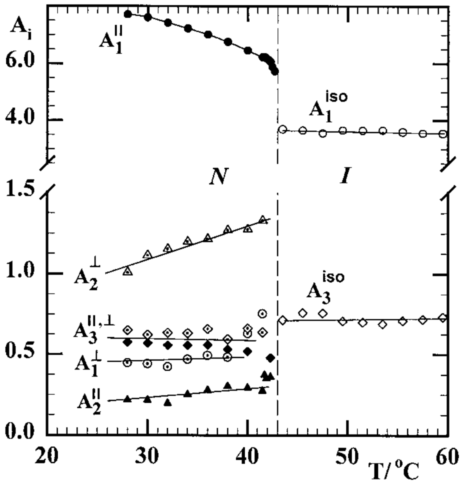

Figure 7. The temperature dependence of the dielectric strengths of the absorption bands corresponding to the different modes of the rotations of 6CHBT molecules.

(ii) A jump in the value of the relaxation time τ_1 (figure 6), corresponding to the molecular rotation around the short axis.

It is worth noticing that the magnitude of the jump of τ_1 depends on the direction of its measurement. The relaxation time $\tau_1^{\perp}$ measured for the configuration $\mathbf{E}\perp\mathbf{n}$ undergoes an essentially smaller jump than $\tau_1^{\|}$ (figure 6). Besides, as we will see later, the activation energy, derived from the temperature dependence of $\tau_1^{\perp}$, is also considerably smaller than that obtained for $\tau_1^{\|}$.

The molecular rotation around the short axis is the only movement which shows differences when investigated with $\mathbf{E}\|\mathbf{n}$ and $\mathbf{E}\perp\mathbf{n}$. The reason seems to be simple, because for $\mathbf{E}\perp\mathbf{n}$ the coupling between the molecular dipole moment and the probing electric field vanishes and rotating molecules are subjected to the nematic potential only. This means that for the estimation of the nematic potential on the basis of the activation energy of the dielectric relaxation time τ_1 and that of the viscosity, one should take into account $\tau_1^{\perp}$.

Figure 8 shows the temperature dependence of the viscosity of 6CHBT measured in the isotropic and nematic phases. A sharp decrease of the viscosity is observed at the isotropic to nematic phase transition. This means that in the measuring method used, the nematic flow causes the molecular alignment [13] and finally, for stationary flow, the velocity v is parallel to the director $\mathbf{n}$, and the velocity gradient $\mathrm{d}v/\mathrm{d}x$ is perpendicular to $\mathbf{n}$. In such a situation, the nematic viscosity has the least possible value. In terms of the Mięsowicz viscosity coefficients [14], the nematic viscosity measured in our experiment is close to η_2.

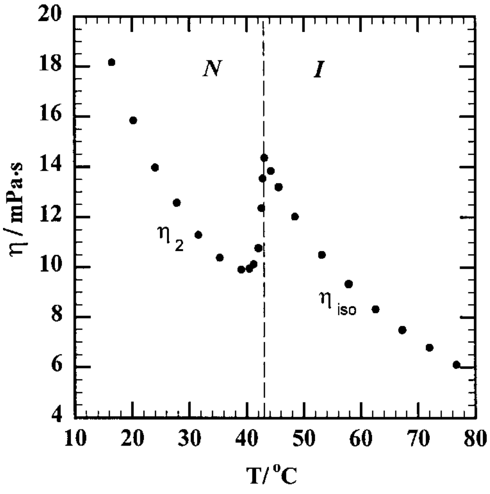

Figure 8. The temperature dependence of the viscosity of 6CHBT measured for the isotropic and nematic phases.

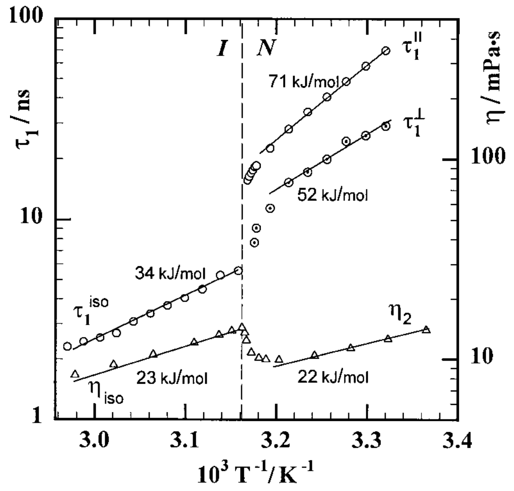

Figure 9. Arrhenius plots for the relaxation time τ_1 and the viscosity. The values of the activation energy are given in the figure.

Figure 9 presents the Arrhenius plots for the relaxation times τ_1 and the viscosity in the isotropic and nematic phases of 6CHBT. The discussion presented above leads to the conclusion that the strength of the nematic potential q can be estimated as a difference between the activation energies for $\tau_1^{\perp}$ and η_2. The value $q = 30\,\mathrm{kJ\,mol^{-1}}$ obtained in our experiment for 6CHBT is typical for the potential strength in other nematics [3].

The data of τ_1^{iso} and η^{iso} obtained for the isotropic phase of 6CHBT can be used for the evaluation of the length of the nematogen molecule in the frame of the Debye model [4]. In the model, the sphere with a radius a represents the rotating dipolar, rigid and axially symmetric molecule of effective length $l = 2a$. The relation between the dielectric relaxation time, corresponding to the molecular rotation around its short axis, and the viscosity of the medium in which the sphere is moving,

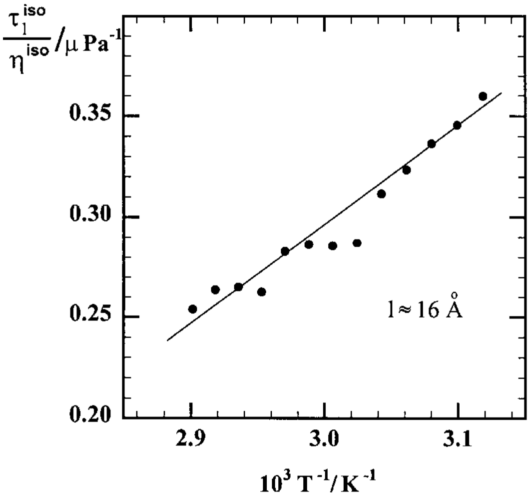

Figure 10. The plot arising from the Debye equation (5) which allows one to estimate the length l of the 6CHBT molecule in the isotropic phase.

has the following form:

$$\tau_1^{\mathrm{iso}} = \frac{4\pi\eta^{\mathrm{iso}}a^3}{kT} \tag{5}$$

where k is the Boltzmann constant and T is the absolute temperature. The slope of the dependence $\tau_1^{\mathrm{iso}}/\eta^{\mathrm{iso}}$ on T^{-1} is proportional to a^3. It is obvious that the Debye model is very simplified and is of rather historical significance. However, as presented on figure 10, the dependence $\tau_1^{\mathrm{iso}}/\eta^{\mathrm{iso}}$ on T^{-1} is, according to equation (5), quite good in linearity; the slope gives a reasonable value $1 \approx 16$ Å for the effective length of the 6CHBT molecule. Quantum-mechanical calculation gives the value of $1 \approx 20$ Å with an all-*trans*-conformation of the $C_6H_{13}-$ group in the 6CHBT molecule.

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