Structural ordering and molecular-optical properties of a discotic liquid crystal (Col$_{ho}$)

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The infrared absorbance and the dispersion of the refractive indices in the region 0.49–0.63 µm of the discotic mesogen 2,3,6,7,10,11-hexaheptyloxytriphenylene were studied for the columnar and isotropic phases. The temperature dependence of the orientational order parameter S and the local field parameters of a light wave acting on the sample have been evaluated. It is shown that the mixing of molecular excitations modifies the behaviour of S as a function of temperature. Molecular-optical properties of the triphenylene derivative, such as the anisotropy of the polarizability, $\Delta\gamma$ and the mean polarizability, $\bar{\gamma}$ were investigated on the basis of the generalized Lorenz–Lorentz relation for uniaxial liquid crystals. The experimentally observed changes of these properties in the columnar phase seem to be affected by the induction mechanism of the change in the molecular polarizability with increasing S.

1. Introduction

The interesting physical properties of the columnar Col$_{h(o,d)}$ phases of discotic mesogens such as one-dimensional electrical conductivity, fast photoconductivity, ferroelectricity, etc. promise numerous technological applications and stimulate extensive studies of these systems [1]. The molecules of these liquid crystals (LCs) consist of a disc-like central core and flexible peripheral aliphatic tails. Information about the long range orientational and translational order parameters of the molecules and their fragments helps to improve our understanding of columnar discotic structures. Studies of the dichroism of polarized IR bands corresponding to the normal molecular modes allow us to determine the order parameters of the molecular fragments [2], as well as the parameters of the anisotropic local field of a light wave acting on these fragments [3]. Because of the complexity of the vibrational spectra of disc-shaped molecules, one has to modify spectral methods for the determination of these parameters. In fact, the local field effects cause the mixing of molecular excitations for adjacent absorption bands, and some new spectral methods to measure the local field parameters have been suggested for discotic phases [4].

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A lack of reliable surfactants for use with columnar phases makes it difficult to attain homogeneous mono-domain samples, as well as to achieve complete IR polarization measurements. Samples produced by Durand's technique [5] cannot be used over the whole temperature region of columnar phases. It is known however that heating of discotic samples does not change the spontaneous homeotropic orientation in the Col$_{ho}$ phase [6]. We show that the behaviour of the order parameter and the parameters of the anisotropic local field as a function of temperature can be obtained from refractometry and the IR spectra of homeotropic samples of these LCs. On the other hand, the mutually consistent nature of the molecular and structural transformations in discotic LCs is manifested by changes in the conformational states within particular LC phases and during phase transitions [7]. Since the disc-shaped molecules of Col$_h$ phases have a large number of aliphatic tails with a variety of conformational states, the molecular polarizability is a sensitive indicator of these changes. However, experimental data on the polarizability of disc-like molecules, and its dependence on the molecular order and the LC phase, are very limited and completely missing for the Col$_h$ phases. The molecular-optical properties, such as the anisotropy of the polarizability $\Delta\gamma$ and the mean polarizability $\bar{\gamma}$ of the columnar discotic liquid crystal Col$_h$, are systematically evaluated in this article.

2. Experimental

The material under investigation is the discotic mesogen 2,3,6,7,10,11-hexaheptyloxytriphenylene (H7T) with the phase sequence Cr–68°C–Col_{ho}–92.5°C–I showing phase transitions between the crystalline, columnar discotic Col_{ho} and isotropic liquid phases. The uniaxial phase Col_{ho} is a two-dimensional hexagonal lattice of molecular columns, perpendicular to this lattice and parallel to the director **n**. The director **n** denotes the preferred axis of orientation of the disc-normals. In the Col_{ho} phase the centres of mass of the molecular cores are translationally ordered along the axes of the columns. The molecular cores have large values of the orientational order parameter $S = \langle 3 \cos^2 \theta_{ln} - 1 \rangle /2$ with respect to **n**, while the disordered aliphatic tails fill the space between the columns. Here, θ_{ln} is the angle between the normal **l** to the core plane and **n**; the angled brackets $\langle ... \rangle$ denote statistical averaging. This material was chosen since the principal components of the Lorentz–factor tensor L_{ii} at fixed temperature far from phase transition Col_{ho}–I were known [4] and a volumetric study had been made as well [8].

To perform the IR spectral measurements over the whole mesophase range, a more reliable means of obtaining homeotropic orientation of the triphenylene derivative was used. Polished fluorite substrates were cleaned by conventional chemical methods and were used for all fabrication without any treatment by surfactants. The monodomain films of the Col_{ho} columnar phase had thickness $d = 5$–$10 \, \mu m$. The uniform homeotropic orientation of the LC with the optic axis oriented normally to substrates was obtained by capillary filling the cell from the isotropic phase, followed by slow cooling of the LC to the operating temperature. Upon orthoscopic observation using the polarizing microscope, a homeotropic sample looked like a black background with irregular individual light point defects in it. The spectra of the absorption bands of H7T samples with homeotropic orientation and in the isotropic phase were obtained using a Fourier transform infrared (FTIR) absorption spectrometer, Vector-22 with multiscanning and subsequent averaging. In cells holding materials in the homeotropic orientation, the light propagated along the optic axis, and we were able to measure the absorption spectrum polarized normal to the director without using a polarizer. This experimental geometry also minimizes the depolarizing effect of multiple scattering of light at fluctuations of the director. The order parameter S is related to the dichroic ratio $N = D_\perp/D_i$ of an isolated IR absorption band, where the $D_{\perp,i}(v_{\perp,i})$ are the integrated optical densities, by the ratio

$$SS_\beta = 1 - Ng. \tag{1}$$

In general the indices $\parallel$, $\perp$, i correspond, respectively, to the direction in the LC which is parallel ($\parallel$) or perpendicular ($\perp$) to the director **n**, and to the isotropic liquid (i). Here we take the given parameter $S_\beta = (3 \cos^2 \beta - 1)/2$, where β is the angle between the transition moment **d** and the molecular axis of symmetry **l**. The correction factor g takes into account the anisotropy of the local field of the light wave [3]:

$$g = \frac{\rho_i n_o}{\rho n_i} \left(\frac{f_i}{f_\perp} \right)^2 \tag{2}$$

where ρ, ρ_i are the densities of the liquid crystal and the isotropic phase, respectively, and $n_{o,i}$ are the background ordinary and the isotropic state refractive indices in the absorption band due to all other vibrational and electronic resonances. The values

$$f_{\parallel,\perp} = 1 + L_{\parallel,\perp}(n_{e,o}^2 - 1) \tag{3}$$

are components of the local field tensor in the absorption band. The parameters $L_{\parallel,\perp}$ are the components of the Lorentz tensor **L**. In the isotropic phase the parameter $f_i = (n_i^2 + 2)/3$.

The dispersion of the refractive indices $n_{e,o,i}$ for treatment of the experimental spectra data is needed. The refractive indices of H7T were measured using a temperature controlled, partially modified [8] Abbé refractometer (Carl Zeiss). This technique is the most convenient one for use with columnar discotics. Easy orientation of the director **n** normal to the surface of the refractometer prisms ensures the observation of two sharp boundary lines, one corresponding to internal reflection angles of the ordinary n_o and the other to the extraordinary n_e refractive indices. To measure refractive indices at other wavelengths in addition to the operating one ($\lambda = 0.589 \, \mu m$) of the refractometer, we applied the intense radiation of a Xe-lamp transmitted through the monochromator. In this case the dispersion compensator was removed from the refractometer and corrections of the refractive indices scale, calibrated relative to the yellow spectral line of a Na-lamp, were made according to ref. [9]. The scale was graduated by using a substance with known refractive indices at chosen wavelengths. Therefore, the temperature dependences of the refractive indices of H7T at wavelengths 0.488, 0.589 and 0.633 μm were obtained. A precision of about 10^{-3} was determined for the refractive indices measured.

3. Results and discussion

The spectra of a homeotropically oriented sample of H7T in the Col_{ho} phase at the reduced temperature $\Delta T = T_c - T = 22.3°C$ and in the isotropic state are shown in figure 1. T_c is the temperature of the columnar–isotropic phase transition. For an investigation of the order parameter S the isolated IR absorption band
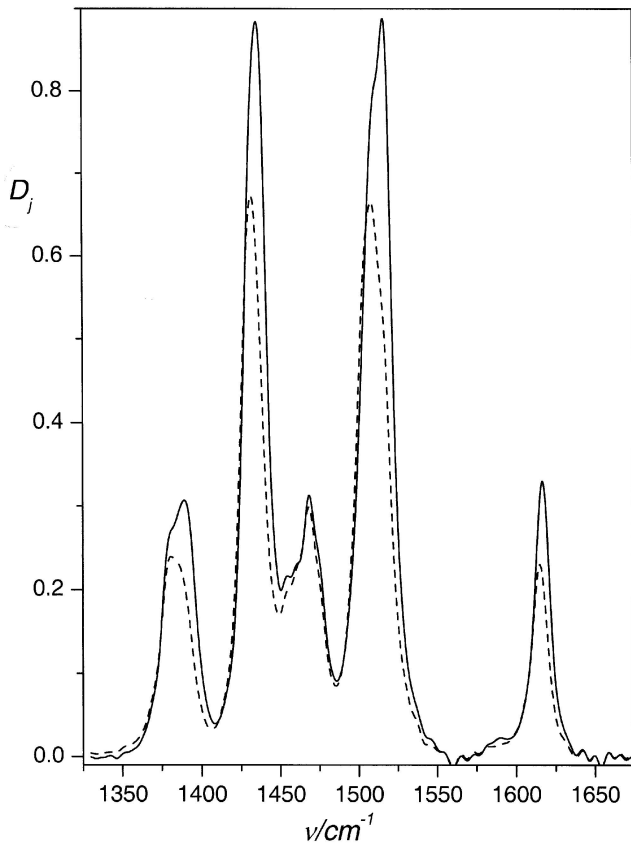
Figure 1. Polarized component $D_\perp(v)$ of the absorption bands of H7T for samples with homeotropic orientation (solid curve) at the reduced temperature $\Delta T = 22.3°C$ and in the isotropic phase (dashed curve), CaF_2 cell, $d = 10\,\mu m$.

$v = 1613.5\,cm^{-1}$ was chosen. It corresponds to the C–C aromatic stretching vibrations of the phenyl rings of the molecular core, which are polarized in the plane of these rings [2]. For the given band parameter S_β is equal to $-1/2$. The order parameter S was determined from equation (1) by replacing the dichroic ratios N by the parameter $N^* = \delta N$, where the correction [4]

$$\delta = \frac{1 + D_\perp^{1507}/D_\perp^{1613}}{1 + D_i^{1507}/D_i^{1613}} \qquad (4)$$

takes into account the mixing of molecular excitations for adjacent absorption bands $v = 1613.5$ and $1507\,cm^{-1}$. The intense band, $v = 1507\,cm^{-1}$, corresponds to the C–C aromatic in-plane deformation, which is polarized in the plane of the phenyl rings. These separated bands in the IR spectra of H7T were fitted to the Gaussian profile, and the integrated optical densities $D_{\perp,i}(v_{\perp,i})$ were used to obtain the temperature dependence of the dichroism and the correction δ. The correction factor δ increases from 0.79 to 0.82 with increasing of temperature.

Temperature dependences of the refractive indices $n_{e,o,i}$ in the columnar and isotropic phases of H7T at three values of the wavelength λ are given in figure 2. The temperature of the specimens was kept constant to $\pm 0.1°$. Below 4°C, near the Col_{ho}–I phase transition, it was not possible to measure the refractive indices, since the corresponding boundary line in the refractometer was not sharp enough. A slight decrease of birefringence, $\Delta n = n_o - n_e$, with increasing temperature reflects a slight decrease in the order parameter of the hexagonal columnar phase. Not long ago, it was revealed that the actual value of Δn for H7T at the Col_{ho}–I transition is 20% higher than the theoretically predicted value [8]. This was verified in several experiments at various wavelengths.

The dispersion of the measured refractive indices, in the Col_{ho} and isotropic phases of H7T can be well approximated by the one-oscillator dispersion relation [10]

$$n_{e,o,i}^2 = 1 + \frac{\lambda^2 A_{\parallel,\perp,i}}{\lambda^2 - B_{\parallel,\perp,i}} \qquad (5)$$

where the values λ are expressed in microns. The parameters A and B depend on the reduced temperature ΔT, the polarization and the approximation interval
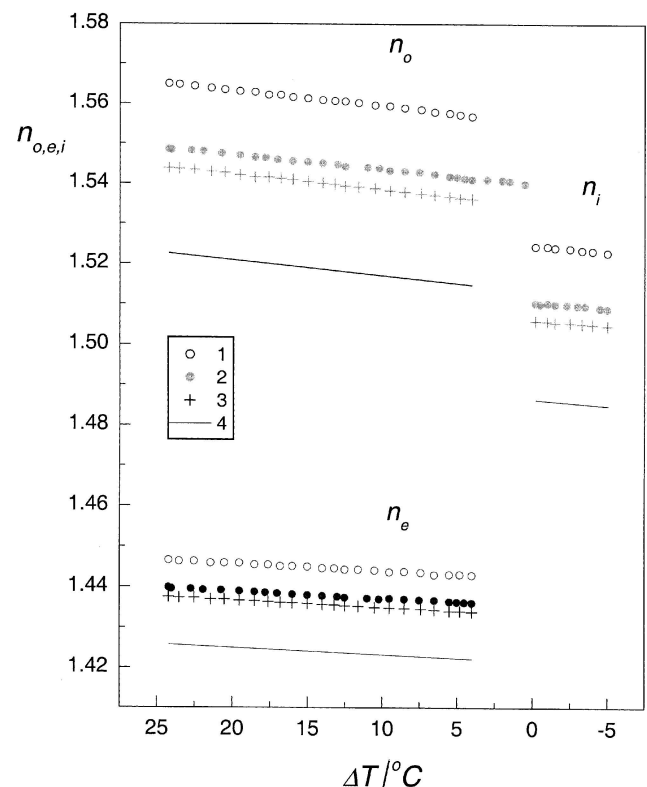

Figure 2. The refractive indices $n_{e,o,i}$ of H7T as a function of temperature at the wavelengths $\lambda = 0.488$ (1), 0.589 (2), 0.633 μm (3). The solid lines (4) show values of $n_{e,o,i}$ calculated from equation (5) for $\lambda = 6.2\,\mu m$.

(λ_j, λ_k). By combining three pairs of values (λ_j, λ_k), from the set $\lambda = 0.488, 0.589, 0.633\,\mu m$, we obtain three pairs of parameters (A_j, B_k) at each fixed temperature ΔT. Then the average values $\bar{A}(\Delta T)$ and $\bar{B}(\Delta T)$ were used to calculate the temperature dependences of the refractive indices $n_{e,o,i}$ at $\lambda = 6.2\,\mu m$ from relation (5). For a weak contribution of vibrational intramolecular resonances to the dispersion of these refractive indices, we can use them as the background for the $v = 1613.5\,cm^{-1}$ absorption band. Temperature dependences of the components $L_{\parallel,\perp}(\Delta T)$ of the Lorentz tensor $\mathbf{L}$, in the Col_{ho} phase of H7T, are calculated from the condition that $L_{\parallel} + 2L_{\perp} = 1$ and the approximation relation

$$\tau(\Delta T) = \frac{\tau_{max}}{\Delta n_{max}}\Delta n(\Delta T) \qquad (6)$$

for the anisotropy of the Lorentz tensor $\tau = 1/3 - L_{\perp}$. Here Δn is the birefringence of the sample at a given temperature of the mesophase. Note that the anisotropy τ, differently from Δn, is wavelength (λ) independent. The parameters τ_{max} and Δn_{max} correspond to a perfectly ordered LC sample $(S = 1)$. This approximation was proposed for uniaxial LCs [11]. Previously the parameter $\tau_{max} = 0.18 \pm 0.01$ and the value $\tau = 0.16 \pm 0.01$ at $\Delta T = 22.3°C$ for H7T were obtained by methods based on self-consistent measurements of the ordering and local field parameters [4]. To determine the unknown parameter Δn_{max} we used the value of Δn measured at the above temperature. Temperature dependences of components of the Lorentz tensor $L_{\parallel,\perp}(\Delta T)$ are given in the inset of figure 3. The component $L_{\perp}$ increases with decreasing ΔT, contrary to what is commonly observed for calamitic LCs. Nevertheless, the anisotropy of the Lorentz tensor decreases with decreasing reduced temperature, since τ is positive for discotic LCs. The values of $L_{\parallel,\perp}(\Delta T)$ and the refractive indices $n_{e,o,i}(\Delta T)$, approximated in the IR region, were used to calculate the background components of the local field tensor and the correction factor g. It is ascertained that the correction factor $g = 1.313 \pm 0.003$ is constant over the whole Col_{ho} phase of H7T.

Figure 3 plots the values of the order parameter S (circles) determined from equation (1) with all corrections, taking into account the anisotropy of the local field and the mixing of molecular excitations for bands $v = 1613.5\,cm^{-1}$ and $v = 1507\,cm^{-1}$. The order parameter S_o (squares) calculated in the approximation of an isotropic local field $(\Delta f = f_{\parallel} - f_{\perp} \approx 0)$ is also shown. The temperature dependences of S and S_o have different characters. As seen in figure 3, the parameter S decreases weakly with increasing temperature from a value of 0.90 ± 0.03 to 0.82 ± 0.05. The behaviour of this parameter corresponds with nuclear magnetic resonance
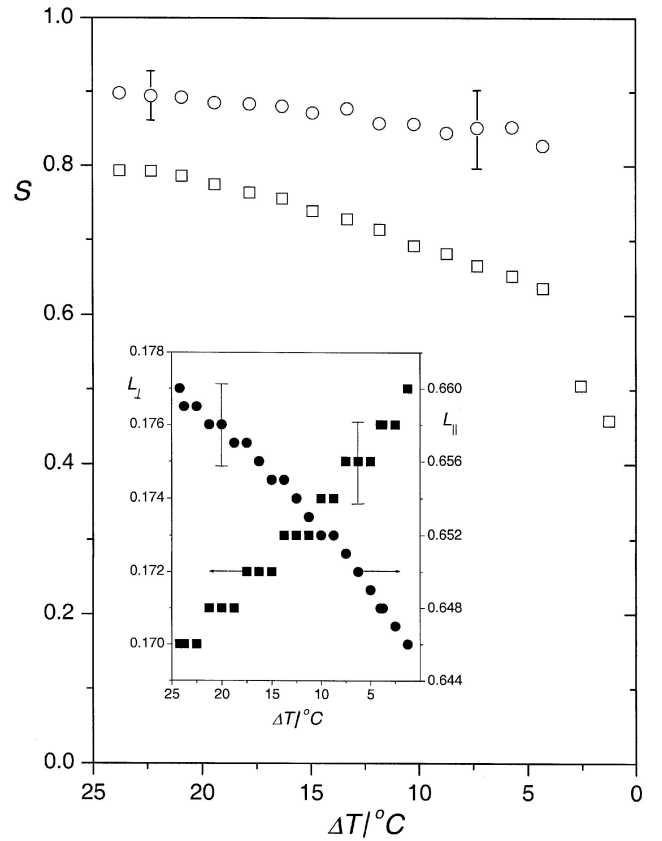

Figure 3. Temperature dependence of the orientational order parameter S in the columnar Col_{ho} phase of H7T. Values of S (circles) are calculated from IR data considering the anisotropy of the local field and the mixing of molecular excitations; values of S_0 (squares) are calculated in the isotropic approximation. Inset: temperature dependence of components of the Lorentz tensor $L_{jj}(\Delta T)$.

(NMR) data obtained for the Col_{ho} phase of H6T [12]. Far from the Col_{ho}–I phase transition at $\Delta T = 22.3°C$, the parameter S_o is 14% less than S, while at $\Delta T = 4°C$ it is 23% less. This means that mixing effects essentially disfigure the temperature behaviour of the orientational order parameter calculated for the chosen absorption band $v = 1613.5\,cm^{-1}$. Below $4°C$ the spectral data are unreliable since the elastic free energy of the discotic LC does not hold a strong homeotropic orientation of the sample. An inspection using the polarizing microscope confirms abnormality of the homeotropic orientation near to the Col_{ho}–I phase transition. Note that a discrepancy in the temperature behaviour of the orientational order parameter calculated for two dipole transition moments was obtained previously for the columnar discotic phase of H7T [13]. The behaviour of S calculated for the stretching band $v = 1613.5\,cm^{-1}$ was related to the effects of disordering of the tails of the disc-shaped molecules in the Col_{ho} phase. However, the temperature curve of S coincides with that of S_o obtained

in the approximation of an isotropic local field. This demonstrates the importance of taking into account the local field effects in studying the absolute orientational order parameter of discotic LCs by spectral methods.

The average longitudinal $\bar{\gamma}_{\parallel}$ and transverse $\bar{\gamma}_{\perp}$ polarizabilities of the molecules relative to the director **n** of the uniaxial LCs can be calculated from the generalized Lorenz–Lorentz equation [14]

$$n_j^2 - 1 = 4\pi N \bar{\gamma}_j f_j \qquad (7)$$

where n_j, f_j are the refractive indices and components of the local field in the j direction. The value $N = \rho N_A / M$ is the number of molecules per unit volume, where M is the molecular mass, N_A is the Avogadro constant and ρ is the density of the mesophase. Then, we have

$$\bar{\gamma}_{\parallel,\perp} = \frac{M(n_{e,o}^2 - 1)}{4\pi \rho N_A [1 + L_{\parallel,\perp}(n_{e,o}^2 - 1)]}. \qquad (8)$$

In order to calculate the main molecular polarizabilities γ_1 and γ_t of the uniaxial disc-shaped molecule with chosen axis **l**, it is necessary to know the order parameter S for the measuring temperature, since $\gamma_t - \gamma_1 = (\bar{\gamma}_{\perp} - \bar{\gamma}_{\parallel})/S$. By making use of this equation and taking into account that $\langle \bar{\gamma} \rangle = (\bar{\gamma}_{\parallel} + 2\bar{\gamma}_{\perp})/3$, $\overline{\Delta\gamma} = \bar{\gamma}_{\perp} - \bar{\gamma}_{\parallel}$ and $\langle \bar{\gamma} \rangle = \bar{\gamma}$, we obtain expressions for γ_1 and γ_t:

$$\gamma_1 = \langle \bar{\gamma} \rangle - \frac{2\overline{\Delta\gamma}}{3S} \qquad (9)$$

$$\gamma_t = \langle \bar{\gamma} \rangle + \frac{\overline{\Delta\gamma}}{3S}. \qquad (10)$$

Figures 4 and 5 give the temperature dependences of $\gamma_{1,t}$, the mean value $\bar{\gamma} = (\gamma_1 + 2\gamma_t)/3$, and the anisotropy $\gamma_a = \gamma_t - \gamma_1$ of the effective polarizability for H7T molecules in the Col_{ho} and isotropic phases, calculated from equations (8)–(10). In the calculations we used the measured values S, $L_{\parallel,\perp}$, $n_{e,o,i}$ at the wavelength $\lambda = 589$ nm and dilatometric data for H7T [8]. At the I–Col_{ho} phase transition, the value of $\bar{\gamma}$ increases discontinuously and in the Col_{ho} phase it changes weakly from 107.30 to 107.65 Å. As seen in these figures, the transverse component γ_t is practically independent of temperature. The longitudinal component γ_1 increases from 63.5 to 66.2 Å with increase in S, since the anisotropy γ_a decreases as S increases. The same character of the temperature dependences of $\gamma_{1,t}$, $\bar{\gamma}$ and γ_a is obtained in the approximation of an isotropic local field. Thus, variations of the polarizability of the molecules are due to the changes in the molecular interactions with increasing S. Nevertheless, these variations are not related to the approximation (6), used for calculating the local field parameters of H7T. Note that the behaviour of the parameters $\gamma_{1,t}$, $\bar{\gamma}$ and γ_a qualitatively corresponds to the mechanism of mutual polarization of the molecules
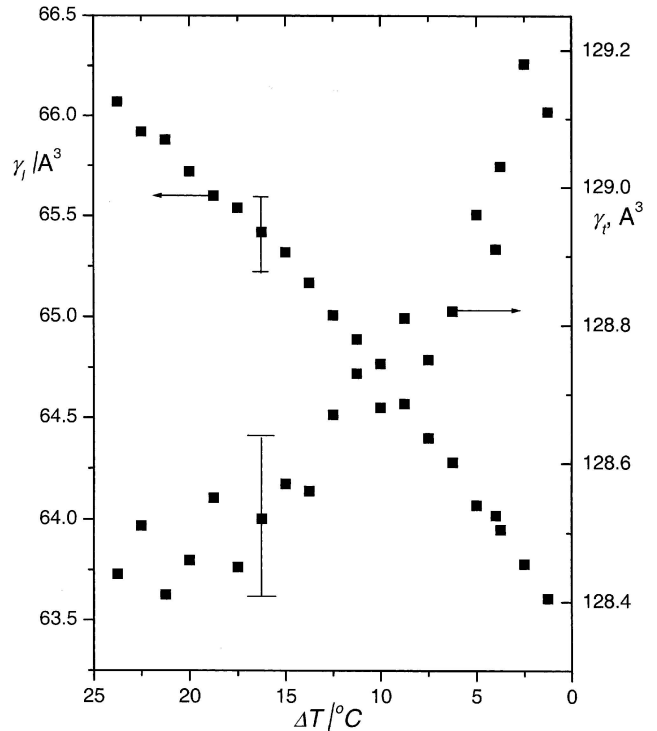

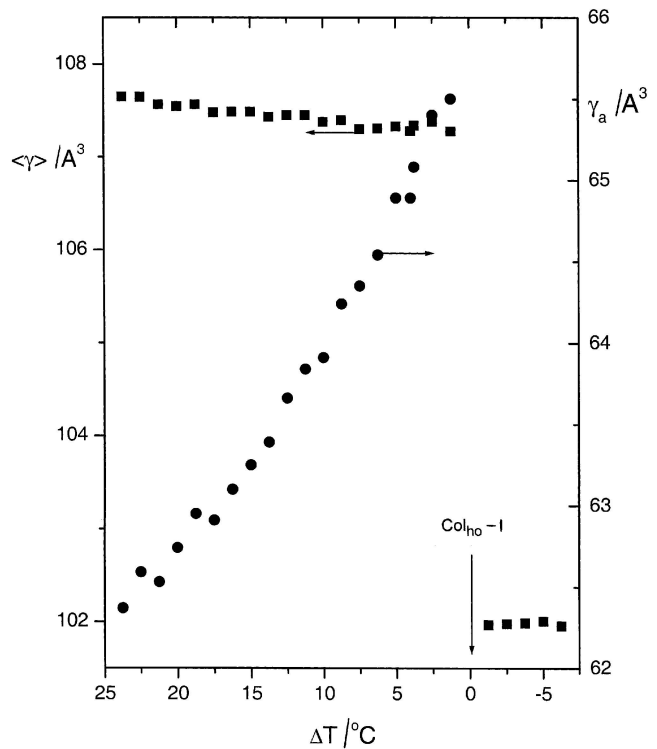Figure 4. Temperature dependences of γ_1 and γ_t in the Col_{ho} phase of H7T.

Figure 5. Temperature dependences of the anisotropy γ_a and the mean value $\bar{\gamma}$ of the molecular polarizability in the columnar and the isotropic phases of H7T.

induced by their relative orientation in the mesophase with increasing S [15]. The anisotropy γ_a of the effective polarizability of the H7T molecules is sensitive to a weak change in orientational ordering of the molecular cores within the columns. The change in the polarizability of the disc-like molecule may be due to variation in the conformational mobility of the aliphatic tails. More detailed information about the contribution of chains to polarizability could be obtained by the approach [7] based on the separation of a discogenic molecule into n fragments, having the polarizability tensors $\gamma^{(F)}$. However, to be able to do this, we need to study the molecular-optical properties for at least one more homologue of these compounds. On the other hand, X-ray studies of columnar discotics [16] do provide evidence for increase in the disorder of the aliphatic chains with increasing temperature. Apparently, in this case one can expect a different character of the dependence of γ_a caused by a change in the conformational states of chains from that which we obtained.

4. Conclusion

To carry out IR polarization measurements, homeotropic samples of the discotic liquid crystal 2,3,6,7,10,11-hexaheptyloxytriphenylene (H7T) were used. It was ascertained that the dispersion of the refractive indices in the visible region is well approximated by the one-oscillator dispersion relation. By combining IR and refractometric data we obtained the temperature dependence of the orientational order parameter and the local field parameters on the basis of approximation (6). It was demonstrated that the mixing of molecular excitations essentially modifies the behaviour of the order parameter as a function of temperature. At the Col_{ho}–I phase transformations and in the columnar phase the experimentally observed changes in the mean value $\bar{\gamma}$ and the anisotropy γ_a are related to the effect of the induction mechanism in changing the polarizabilities of the ordered discogenic molecules. Thus, the results discussed in this paper illustrate the effectiveness of IR spectroscopy and refractometry methods for the investigation of the structure and molecular-optical properties of columnar phases of discotic LCs.

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