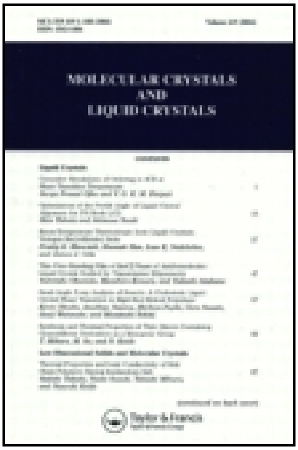

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Orientational Ordering and Polarizability of Molecules in the Columnar Phase of Discotic Liquid Crystal

V. A. Gunyakov [a] & S. M. Shibli [a]

[a] Instituto de Física, Universidade de São Paulo, São Paulo (SP), Brazil

Version of record first published: 18 Oct 2010

To cite this article: V. A. Gunyakov & S. M. Shibli (2004): Orientational Ordering and Polarizability of Molecules in the Columnar Phase of Discotic Liquid Crystal, Molecular Crystals and Liquid Crystals, 409:1, 409-420

To link to this article: http://dx.doi.org/10.1080/15421400490433785

Mol. Cryst. Liq. Cryst., Vol. 409, pp. 409–420, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490433785

ORIENTATIONAL ORDERING AND POLARIZABILITY OF MOLECULES IN THE COLUMNAR PHASE OF DISCOTIC LIQUID CRYSTAL

V. A. Gunyakov[a] *and S. M. Shibli*
Instituto de Física, Universidade de São Paulo, Caixa Postal 66318,
05389-970, São Paulo (SP), Brazil

The structural and molecular-optical properties of the columnar discotic liquid crystal 2,3,6,7,10,11-hexaheptyloxytriphenylene were studied by using of refractometric and infrared (IR) measurements. Temperature dependence of the orientational order parameter S with allowance for the anisotropy of the local field of a light wave and mixing of molecular excitations was evaluated for C–C aromatic stretching band. The local field parameters have been evaluated within approximation of the effective spheroidal Lorentz cavity model. The anisotropy γ_a *and the mean value* $\overline{\gamma}$ *of the molecular polarizability of triphenylene were investigated for several wavelengths. The experimentally observed changes of molecular-optical properties in columnar phase seem to be affected by the induction mechanism of the variety of the molecular polarizability with increasing of S, proposed previously for calamitic liquid crystals. Furthermore, these properties are not related to the effects of aliphatic tails disordering.*

1. INTRODUCTION

The interesting physical properties of the columnar $D_{h(o,d)}$ phases of discotic liquid crystals (LC's) such as one-dimensional electrical conductivity, fast photoconductivity, ferroelectricity, etc., promise numerous technological applications and stimulate the extensive studies of these objects [1]. Molecules of these LC's consist of a disc-like central core and flexible

---

The authors acknowledge Fundação de Amparo à Pesquisa de São Paulo (FAPESP) for financial support.

[a] Permanent address: L. V. Kirenski Institute of Physics, Siberian Branch of the Russian Academy of Science 660036 Krasnoyarsk, Russia.

Address correspondence to S. M. Shibli, Instituto de Fisica, Universidade de São Paulo, Caixa Postal 66318, 05389-970, São Paulo (SP), Brazil. E-mail: shibli@if.usp.br

aliphatic tails. The information about the long-range orientational and translational order parameters of the molecules and their fragments improve our understanding of columnar discotic structures. The study of dichroism of polarized IR bands corresponding to the normal molecular modes allows 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]. Besides, the local field effects cause the mixing of molecular excitations for adjacent absorption bands and have to modify spectral methods for experimental determination of these parameters in discotic LC's [4]. At the same time, it would be interesting to check validity of the modeling approaches for determination of the anisotropic local field in the discotic phases. We show that the local field parameters can be evaluated within approximation of the effective spheroidal Lorentz cavity model. On the other hand, the mutually consistent nature of molecular and structural transformations in discotic LC's is manifested by changes of conformational states within particular LC phases and under phase transitions. Since disc-shaped molecules 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's phases are very limited. So far the polarizability of discogenic molecules in the reentrant nematic phase N_{DR} was investigated [5]. The temperature behavior of the polarizability was related to the effects of molecular aliphatic tails disordering. The influence of the translational ordering of molecules in columns on the molecular-optical properties is not elucidated for discotic phases. In this paper we systematically evaluated the mean value $\overline{\gamma}$ and the anisotropy γ_a of the molecular polarizability of the columnar discotic for several wavelengths, with allowance for anisotropy of the local field and in the isotropic approximation.

2. EXPERIMENTAL

The object of investigation is the discotic liquid crystal 2,3,6,7,10,11-hexaheptyloxytriphenylene (H7T) with the temperature sequence Cr- 68°C - D_{ho}- 92.5°C - I of the phase transitions between crystal, columnar discotic D_{ho} phases, and isotropic liquid. The uniaxial phase of D_{ho} is two-dimensional hexagonal lattice of molecular columns, which are perpendicular to this lattice and parallel to the director **n** [6]. The director **n** denotes the preferred axis of orientation of the disc-normal. In the D_{ho} phase the centers 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 $S = \langle 3\cos^2\theta_{\mathrm{ln}} - 1\rangle/2$ 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**, and angle brackets $\langle ... \rangle$ denote statistical averaging.

To perform IR spectra measurements within whole mesophase more reliable homeotropic orientation of triphenylene were used. The preparation of the sample was same as in [4]. The spectra of the absorption bands of the H7T were obtained by Fourier transform infrared absorption (FTIR) spectrometer Vector-22 with multiscanning and subsequent averaging. In the sample holders the molecules are in a homeotropic orientation, where the light propagates along the optical axes, that enable us 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 dichroic ratio $N = D_\perp / D_i$ of isolated IR absorption band, where $D_{\perp,i}(\nu_{\perp,i})$-integrated optical densities, by the ratio

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

In general the indices $||$, $\perp$, I correspond to direction of LC which are parallel ($||$), perpendicular ($\perp$) to the director **n** and 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 densities of the liquid-crystal and isotropic phase, $n_{o,i}$ are background ordinary and isotropic state refractive indices in the absorption band due to all other vibrational and electronic resonances. The values

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

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

3. RESULTS AND DISCUSSION

We measured the dichroic ratio $N = D_\perp / D_i$ of liquid crystal sample with homeotropic orientation for IR absorption band $\nu = 1613.5\,\mathrm{cm}^{-1}$. It corresponds to the C–C aromatic stretching vibrations of phenyl rings of the molecular core, which are polarized in the plane of these rings [2]. For given band parameter S_β is equal to $-1/2$. The temperature dependence of N is shown in Figure 1. The order parameter S was determined from Eq. (1) by replacing the dichroic ratios N by the parameter $N^* = \delta N$, where the correction [4]

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

takes into account the mixing of molecular excitations due to resonance interaction between molecules. The adjacent intense band $\nu = 1507\,\mathrm{cm}^{-1}$ corresponds to the C–C aromatic in-plane deformation, which is polarized in the plane of phenyl rings. These separated bands were fitted to the Gaussian profile, and the integrated optical densities $D_{\perp,i}(\nu_{\perp,i})$ were used

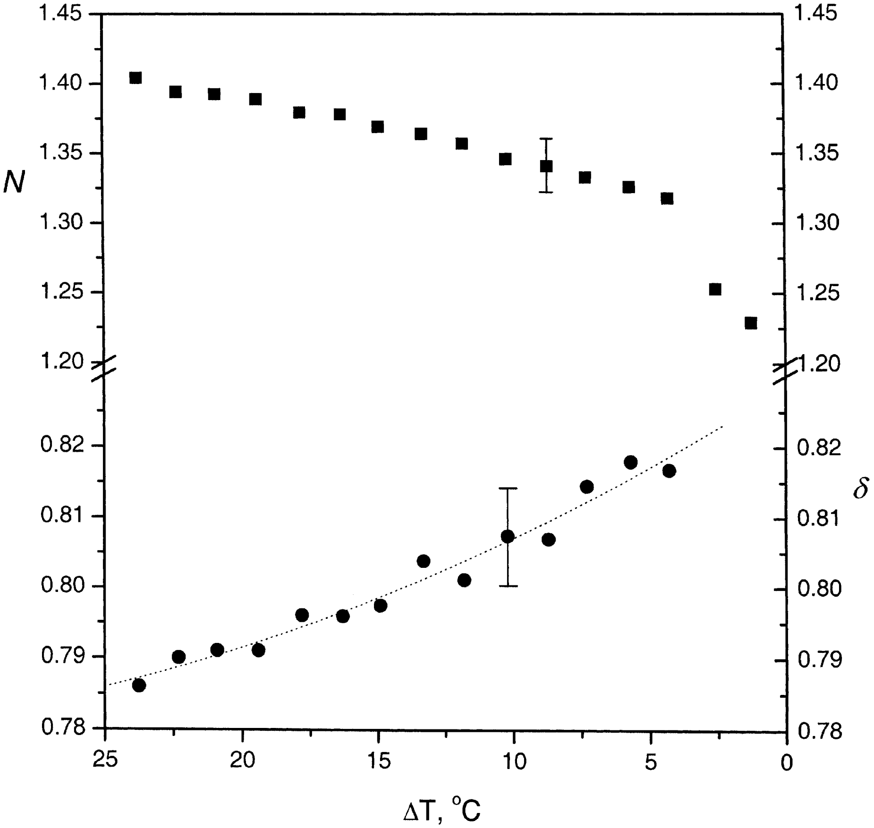

FIGURE 1 Temperature dependence of the dichroic ratio $N = D_\perp(\nu)/D_i(\nu)$ for the $\nu = 1613.5\,\mathrm{cm}^{-1}$absorption band and the correction factor δ.

for obtaining of temperature dependence of dichroism and the correction δ. As seen from Figure 1 the correction factor δ increase from 0.79 till 0.82 with increasing of temperature. Note that for the diluted solution of H7T this factor is equal to unity.

Dispersion of the refractive indices $n_{e,o,i}$ for treatment of spectral experimental data is needed. The refractive indices of triphenylene at wavelengths of 0.488, 0.589 and 0.633 μm were obtained by a temperature controlled, partially modified [7] Abbe refractometer (Carl Zeiss). Precision of about 10^{-3} was determined to the refractive indices measurements. The temperature dependencies of the refractive indices $n_{e,o,i}$ in the columnar and isotropic phases of H7T are given in Figure 2. The accuracy of the

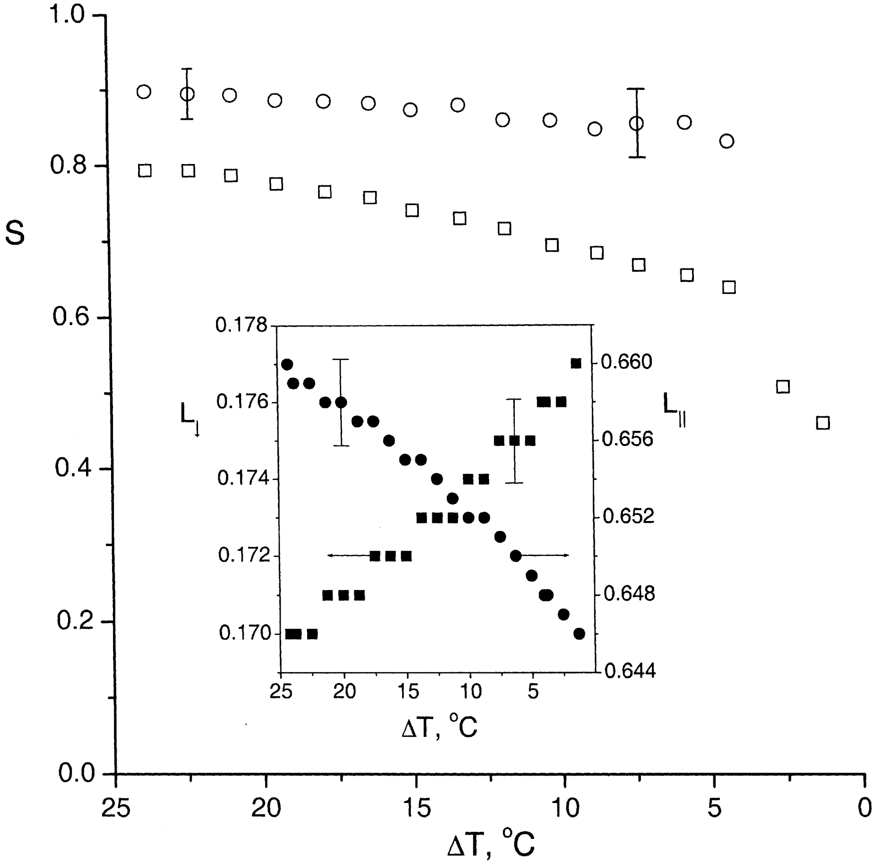

FIGURE 2 The refractive indices $n_{e,o,i}$ of H7T as a function of the temperature at the wavelengths $\lambda = 0.488$ (1), 0.589 (2), 0.633 μm (3). The solid lines (4) show values of $n_{e,o,i}$ calculated from eq. 5 for $\lambda = 6.2$ μm.

temperature of the specimens was kept constant to ±0.1°. The optical anisotropy $\Delta n = n_o - n_e$ is negative as expected for disc-like polyaromatic molecules. A slight decrease of Δn with increasing of temperature originated from slight decrease of S in columnar phase. An experimental value of Δn at the D_{ho}-I transition is 20% higher than that predicted by the empirical relation

$$\frac{\overline{n^2} - 1}{\rho(\overline{n^2} + 2)} = \frac{n_i^2 - 1}{\rho_i(n_i^2 + 2)}. \tag{5}$$

Here $\overline{n^2} = (n_e^2 + 2n_o^2)/3$. The explanation of this fact can be obtained by studying of the features of the polarizability variations at D_{ho}-I transition.

A model discussed elsewhere [8] was used for determining the magnitude and temperature dependence of the components $L_{||,\perp}$, of the Lorentz tensor $\mathbf{L}$, in the columnar phase of H7T. In this model assumed that disk-like molecule is in an effective Lorentzian cavity. The shape of the cavity is determined by the orientational-statistics properties of the mesophase. If $S = 1$, the shape of the cavity corresponds to a molecular spheroid. If $S \neq 1$, the short axis of the cavity is along the director $\mathbf{n}$, the cavity is less anisotropic in shape than is the molecule. In this case temperature dependence of the anisotropy of the Lorentz tensor $\tau = 1/3 - L_\perp$ can be approximated by

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

Here Δn is the birefringence of the sample at a given temperature of the mesophase. Note that the anisotropy τ, differently of Δn, is wavelength (λ) independent. The parameters $\tau_{\max}$ and $\Delta n_{\max}$ correspond to a perfectly ordered LC sample ($S = 1$). 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 $\Delta n_{\max}$ we used the value Δn measured at the above temperature. The components $L_{||,\perp}$ of the Lorentz tensor $\mathbf{L}$, in the D_{ho} phase of H7T, are calculated from the condition that $L_{||} + 2L_\perp = 1$ and the approximation (6). Temperature dependencies of these parameters are given in the insert of Figure 3. The component $L_\perp$ increases with decreasing of ΔT contrary to what is commonly observed for calamitic LC's. Nevertheless, the anisotropy of the Lorentz tensor decreases with decreasing of reduced temperature, since τ is positive for discotic LC's.

To obtain the background refractive indices at $\lambda = 6.2$ μm we used simple dispersion relation $n_{e,o,i}^2 = 1 + \lambda^2 A_{||,\perp,i}/(\lambda^2 - B_{||,\perp,i})$ [9], where the values of λ are expressed in microns. The parameters A and B depend

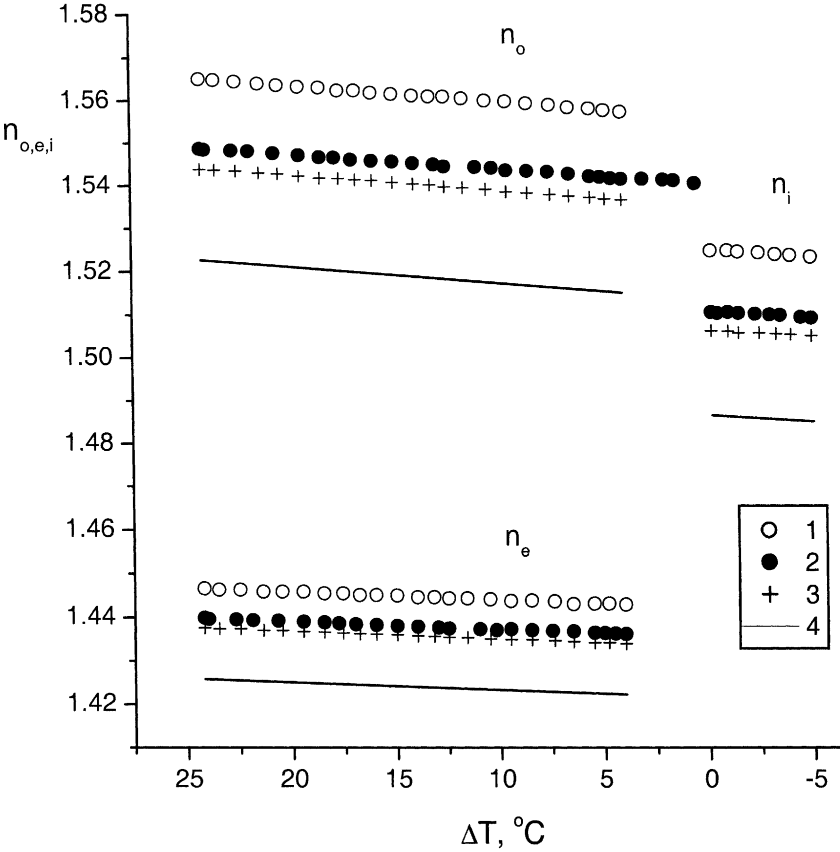

FIGURE 3 Temperature dependence of the orientational order parameter S at the columnar discotic D_{ho} phase of triphenylene. Values of S (circles) calculated from IR data considering the anisotropy of the local field and the mixing of molecular excitations and values of S_o (squares) calculated in the isotropic approximation are shown. Insert: temperature dependence of componentsof the Lorentz tensor $L_{jj}(\Delta T)$.

on the reduced temperature ΔT, the polarization and the approximation interval $(\lambda_j,\ \lambda_k)$. The values of $L_{\|,\perp}$ and refractive indices $n_{e,o,i}$ approximated in IR region were used to calculate the background components $f_{\|,\perp}(\Delta T)$ of the local field tensor (3) and the correction factor g (2). The correction factor $g = 1.313 \pm 0.003$ is kept constant within whole D_{ho} phase of triphenylene.

In Figure 3 the values of the order parameter S (circles) determined from Eq. (1) with all corrections are shown, taking into account the anisotropy of the local field and the mixing of molecular excitations for bands

$\nu = 1613.5\,\text{cm}^{-1}$ and $\nu = 1507\,\text{cm}^{-1}$. The order parameter S_o (squares) calculated in the approximation of isotropic local field $f_{||,\perp} = (\overline{n^2} + 2)/3$ and in agreement to the relation (5) is also shown. In this case we have the correction factor $g = 1$. From the abnormality of the relation (5) we obtain the correction factor $g < 1$ and very low values of the order parameter of about 0.5. Taking into account the anisotropy of the local field only leads us to nonphysical values of the order parameter $S > 1$. As seen in Figure 3 the temperature dependencies of S and S_o have different character. The parameter S weakly decreases with increasing of temperature from value of 0.90 ± 0.03 till 0.82 ± 0.05. The behavior of this parameter corresponds to the nuclear magnetic resonance (NMR) data obtained for the D_{ho} phase of the H6T homologue [10]. Far from the D_{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%. It means that mixing effects essentially disfigure temperature behavior of the orientational order parameter calculated for chosen absorption band $\nu = 1613.5\,\text{cm}^{-1}$. Below 4°C the spectral data is not reliable since an elastic free energy of discotic LC does not hold strong homeotropic orientation of the sample. An inspection under polarizing microscope confirms the fact of abnormality of homeotropic orientation near to the D_{ho}-I phase transition. Note that the discrepancy of the temperature behavior of orientational order parameter calculated for two dipole transition moments was obtained previously for columnar discotic H7T [11]. The behavior of S calculated for the stretching band $\nu = 1613.5\,\text{cm}^{-1}$ was related to the effects of tails disordering of disc-shaped molecules in the D_{ho} phase. However, the temperature curve of S coincides with one of S_o obtained in the approximation of isotropic local field. This demonstrates the importance in taking into account the local field effects for studying the absolute orientational order parameter of the discotic LC's by spectral methods.

To calculate the main molecular polarizabilities γ_l and γ_t of uniaxial disk-shaped molecule with chosen axis **l** we used expressions

$$\gamma_l = \langle\overline{\gamma}\rangle - \frac{2\overline{\Delta\gamma}}{3S}, \quad \gamma_t = \langle\overline{\gamma}\rangle + \frac{\overline{\Delta\gamma}}{3S}, \tag{7}$$

where $\langle\overline{\gamma}\rangle = (\overline{\gamma}_{||} + 2\overline{\gamma}_{\perp})/3$ and $\overline{\Delta\gamma} = \overline{\gamma}_{\perp} - \overline{\gamma}_{||}$. The average longitudinal $\overline{\gamma}_{||}$ and transverse $\overline{\gamma}_{\perp}$ polarizabilities of the molecules relative to the director **n** of the uniaxial liquid crystalline phase calculated from [12]

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

Here M is the molecular weight, N_A is the Avogadro constant and ρ is the density of the mesophase. In the isotropic approximation $\Delta f = 0$ for H7T the mean value $\bar{\gamma}$ of polarizability is defined as [5]

$$\bar{\gamma} = \frac{3M(\overline{n^2} - 1)}{4\pi N_A \rho[\overline{n^2} - 2(n_o^2 - n_e^2)\tau_k + 2]}, \quad \tau_k = \frac{Q}{9(1 - Q/3)}, \tag{9}$$

where $Q = (n_o^2 - n_e^2)/(\overline{n^2} - 1)$. On the other hand in the approximation of the isotropic tensor **f** the relation

$$S(T)\frac{\gamma_a}{\bar{\gamma}} = \frac{n_o^2 - n_e^2}{\overline{n^2} - 1} \tag{10}$$

is valid. Figures 4 and 5 give the temperature dependencies of the mean value $\bar{\gamma} = (\gamma_l + 2\gamma_t)/3$ and anisotropy $\gamma_a = \gamma_t - \gamma_l$ of effective polarizability

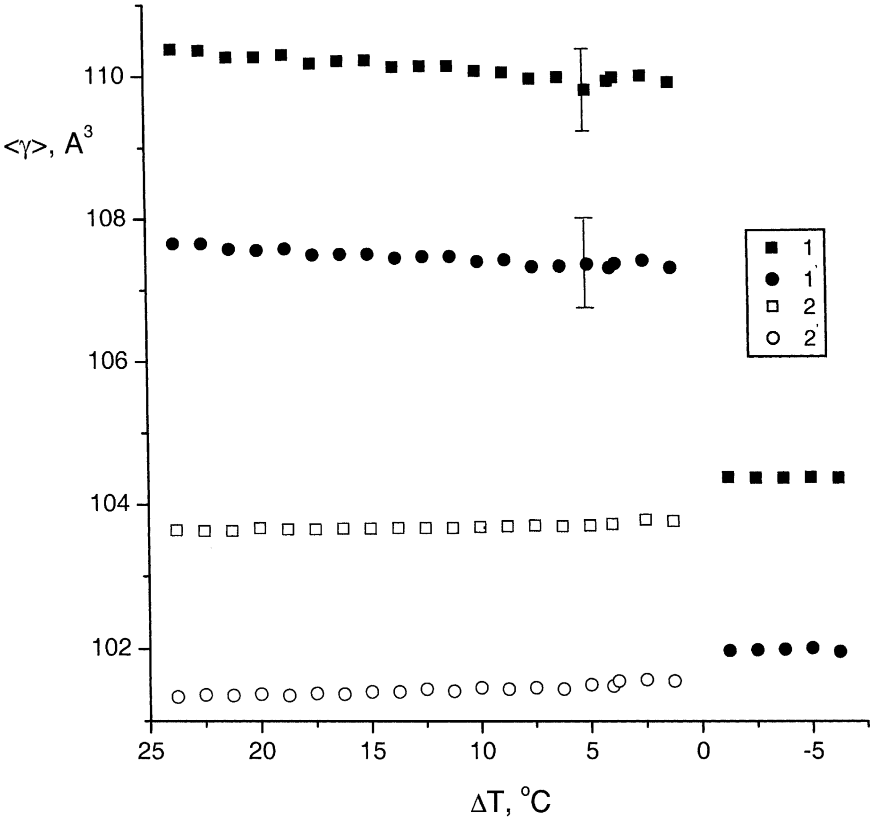

FIGURE 4 Temperature dependence of $\bar{\gamma}$ in the columnar phase D_{ho} of H7T. 1, 2 and 1′, 2′ Experimental values for $\lambda = 0.488$ and $0.589\,\mu$m were found with allowance for the anisotropy of the local field (1, 1′) and in the isotropic approximation (2, 2′), respectively.

for H7T molecules in the D_{ho} and isotropic phases, calculated from Eqs. (7)–(10). In the calculations we used the measured values S, $L_{\|,\perp}$ and $n_{e,o,i}$ at the wavelengths $\lambda = 0.488$, $0.589\,\mu\mathrm{m}$ for H7T. As seen in Figures 4 and 5, at the I-D_{ho} phase transition, the value of $\bar{\gamma}$ increases discontinuously, but in the D_{ho} phase it is practically independent of the temperature within experimental error. The anisotropy γ_a of the polarizability of disc-shaped molecules increases with the increase of temperature. The use of the isotropic approximation (9)-(10) gives low value of γ_a and a value of $\bar{\gamma}$ which a weak dependence of the phase state. The behavior of $\bar{\gamma}$ and γ_a, calculated in the approximation of isotropic local field, demonstrates that variations of the polarizability are due to the changes in the molecular interactions with increasing of S. Nevertheless, these

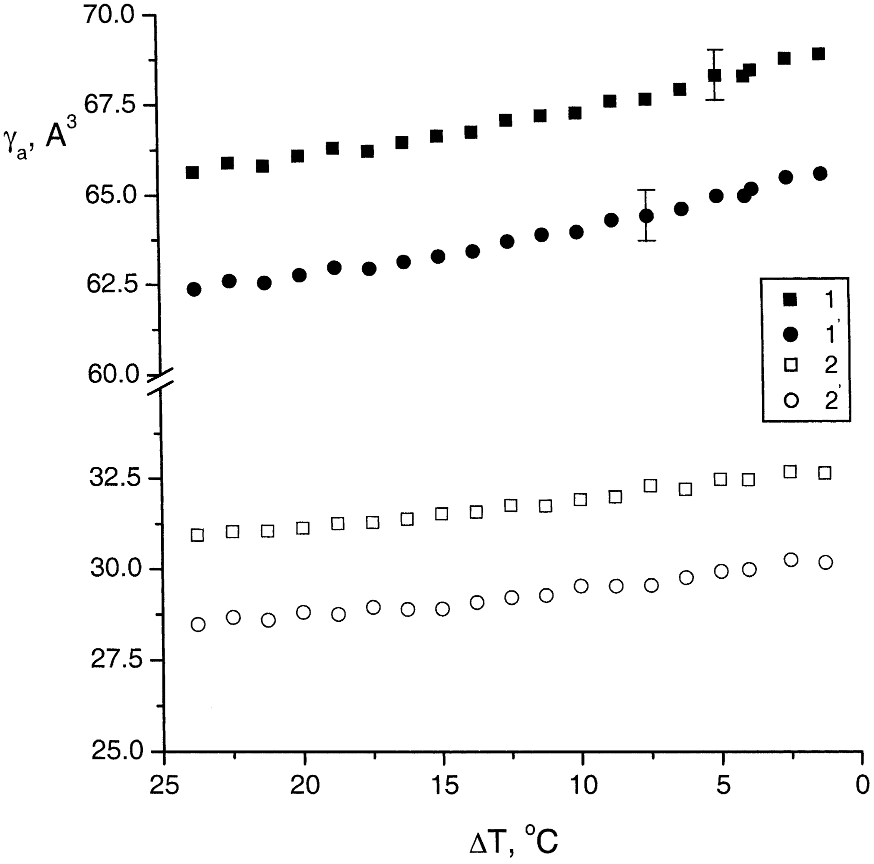

FIGURE 5 Temperature dependence of γ_a in the columnar phase D_{ho} of H7T. The notation is the same as in Figure 4.

variations are not related to the approximation (6), used for calculating the local field parameters of triphenylene. Note that the behavior of the parameters $\overline{\gamma}$ and γ_a qualitatively corresponds to the mechanism of the mutual polarization of the molecules induced by their relative orientation in the mesophase with increasing of S [13]. The anisotropy γ_a of the effective polarizability of H7T molecules is sensitive to a weak change of orientational ordering of the molecular cores within the columns. The change of the polarizability in columnar phase may be due to a variation in the conformational mobility of the aliphatic tail chains, since X-ray data [14] evidence about the increase of the disorder of these chains with increasing temperature. But in this case we can expect different characters of the dependence of γ_a and $\overline{\gamma}$ that we obtained. Apparently, this mechanism dominates in the behavior of polarizability in case of discoid nematics.

4. CONCLUSION

The temperature dependence of orientational order parameter and the local field parameters of the columnar discotic liquid crystal H7T were studied by combining IR and refractometric data. An abnormality of empirical relation (5) at D_{ho}-I phase transition was confirmed for several wavelengths. This abnormality leads to unjustified low value of the orientational order parameter for columnar phase and demonstrates the importance to take into account the local field effects. The same character of the temperature dependencies of γ_a and $\overline{\gamma}$, calculated with allowance for the anisotropy of the local field and in the isotropic approximation, shows the validity of applying of the effective spheroidal Lorentz cavity model and relation (6) for columnar discotic phase. By using the approximation of the isotropic tensor **f** considerably reduced value of γ_a is obtained in columnar phase.The experimentally observed changes in the mean value $\overline{\gamma}$ and the anisotropy γ_a are related to the induction mechanism of the change in the polarizabilities of ordered molecules, proposed previously for calamitic LC's. Thus, in spite of relative weak variety of the orientational order parameter in the columnar phase of H7T spectral technique is sensitive and it allows us to obtain information about features of the change of the molecular polarizability in discotic phases.

REFERENCES

[1] Chandrasekhar, S. & Krishna Prasad, S. (1999). Recent developments in discotic liquid crystals, *Contemp. Phys.*, *40*, 237–245.

[2] Kruk, G., Kocot, A., Wrzalik, R., Vij, J. K., Karthaus, O., & Ringsdorf, H. (1993). Infrared absorption study of hexapentyloxytriphenylene discotic liquid crystal. *Liq. Cryst.*, *14*, 807–819.

[3] Aver'yanov, E. M. & Osipov, M. A. (1990). Effects of the local field of a light wave in the molecular optics of liquid crystals. *Sov. Phys. Usp.*, *33*, 365–384, Errata:of the paper mentioned in ref.3. *Sov. Phys. Usp.* (1990), *33*, 880.

[4] Aver'yanov E. M., Gunyakov, V. A., Korets, A. Y., & Akopova, O. B. (2000). Spectral features of polarized light absorption and anisotropy of a local field in the Dho discotic. *Opt. Spectrosc.*, *88*, 891–897.

[5] Aver'yanov, E. M. (1997). Orientational ordering, conformation and polarizability of molecules in the reentrant phase of discoid nematics. *J. Struct. Chem.*, *35*, 71–77.

[6] Chandrasekhar, S. (1993). Discotic Liquid Crystals: A brief review. *Liq. Cryst.*, *14*, 3–14.

[7] Gunyakov, V. A., Shestakov, N. P., & Shibli, S. M. (2003). Density and refractive index measurements in hexaheptyloxytriphenylene discotic liquid crystal. *Liq. Cryst.* in the press.

[8] Aver'yanov, E. M., Zhuikov, V. A., Zyryanov, V. Y., & Shabanov, V. F. (1984). Anisotropy of local field in uniaxial liquid crystals. *Sov. Phys. JETP*, *59*, 1227–1233.

[9] Wu, S. T. (1991). A semiempirical model for liquid-crystal refractive index dispersions. *J. Appl. Phys.*, *69*, 2080–2087.

[10] Shen, X., Dong, R. Y., Boden, N., Bushby, R. J., Martin, P. S., & Wood, A. (1998). Orientational ordering and dynamics in the columnar phase of a discotic liquid crystal studied by deuteron NMR spectroscopy. *J. Chem. Phys.*, *108*, 4324–4332.

[11] Orgasinska, B., Kocot, A., Merkel, K., Wrzalik, R., Ziolo, J., Perova, T., & Vij, J. K. (1999). Infrared study of the orientational order of the mesogen in discotic phases of hexapentyloxytriphenylene and hexaheptyloxytriphenylene. *J. Mol. Struct.*, *511–512*, 271–276.

[12] Dunmur, D. A. (1998). Physical origin of liquid crystal optical properties. In: *The Optics of Thermotropic Liquid Crystals*, Taylor & Francis: London, 5–40.

[13] Aver'yanov, E. M. & Shabanov, V. F. (1981). Structural order and molecular polarizability in uniaxial liquid crystals. *Sov. Phys. Crystallogr.*, *26*, 96–98.

[14] Fontes, E., Heiney, P. A., Ohba, M., Haseltine, J. N., & Smith, A. B. (1988). Molecular disorder in columnar-phase discotic liquid-crystal strands. *Phys. Rev. A*, *37*, 1329–1334.