Molecular Crystals and Liquid Crystals

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

Conformation and Electronic Structure Studies of Molecules at the Col HO - I Phase Transition in Columnar Discotic Liquid Crystal

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

[a] Instituto de Física, Universidade de São Paulo Caixa, São Paulo (SP), 66318, 05389-970, Brazil

Version of record first published: 18 Oct 2010

To cite this article: V. A. Gunyakov & S. M. Shibli (2003): Conformation and Electronic Structure Studies of Molecules at the Col HO - I Phase Transition in Columnar Discotic Liquid Crystal, Molecular Crystals and Liquid Crystals, 397:1, 273-283

To link to this article: http://dx.doi.org/10.1080/714965594

Mol. Cryst. Liq. Cryst., Vol. 397, pp. 273/[573]–283/[583], 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390214202

CONFORMATION AND ELECTRONIC STRUCTURE STUDIES OF MOLECULES AT THE Col_{ho}-I PHASE TRANSITION IN COLUMNAR 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 changes of the electronic structure of molecules in the columnar discotic liquid crystal 2,3,6,7,10,11-hexaheptyloxytriphenylene were studied by using the polarized electronic absorption measurements. The detailed analysis of the spectral data showed that a mixing of electronic excitations is present in discotics and that it affects the measured values of the optical density and the oscillator strength of the electronic absorption bands. The changes in the oscillator strength of the long-wavelength electronic transition and the conformation of the aromatic molecular cores have been discovered experimentally upon the isotropic – columnar phase transition.

Keywords: electronic absorption spectra; columnar phases; discotic liquid crystals

INTRODUCTION

Molecules of discotic columnar and discotic nematic liquid crystals (LCs) consist of a disc-like aromatic central core and flexible aliphatic tails [1]. The study of the conformational changes of both the flexible tails and the rigid core of molecules in different discotic liquid-crystal phases is of considerable interest for conformational analysis. The evidence from the refraction measurements indicates that in discotic LC the conformational state of flexible tails depends on the length, type and degree of ordering of molecules, and the change in the conformational state of tails has effect on

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

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

*Corresponding author. Tel: 55-11-3091-6721, Fax: 55-11-3091-6715, E-mail: shibli@if.usp.br

the character of the phase transitions [2]. The same level of understanding that exist for the aliphatic tails lacks for the rigid core, since there are no previous study on the qualitative data of the conformational changes at the core of molecules in a discotic. The investigations of the changes in the electronic structure of molecules, in particular, in transition oscillator strength, by the orientational and translational ordering of molecules in the discotic phases and at the phase transitions are still sparse [3,4]. On the other hand, the relationship between the electronic structure and the conformation of the π-conjugation organic fragments of the molecular cores has been studied for the calamitic LCs [5]. Therefore, the use of the parameters of the electronic structure of molecules, as an indicator of their conformational changes in discotics, seems promising.

Neutron-diffraction studies of the structure of the discogenic triphenylene molecules showed that the planes of the outer phenyl rings of the molecular core are not coplanar with each other and with the plane of the central ring, because of the steric effects of hydrogen atoms bonded with aromatic carbon atoms [6]. The change of the angles between outer and the central phenyl rings may be the most probable kind of conformational modification. In the present work we have performed electronic absorption measurements to study the changes in electronic structure and the conformation of the molecular cores in a mesogenic compound of triphenylene, as a function of temperature in the columnar and isotropic phases.

EXPERIMENTAL

The sample studied is the 2,3,6,7,10,11-hexaheptyloxytriphenylene (H7T) discotic LC with the temperature sequence $Cr\text{-}68^{\circ}C\text{–}Col_{ho}\text{-}92.5^{\circ}C\text{-}I$ of the phase transitions between crystal, columnar discotic phase and isotropic liquid. The uniaxial phase of Col_{ho} is two-dimensional hexagonal lattice of molecular columns, which are 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 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 $S = \langle 3\cos^2\theta_{\ln} - 1\rangle/2$ with respect to **n**, while the disordered aliphatic tails fill the space between the columns. Here, $\theta_{\ln}$ is the angle between the molecular axis of symmetry **l**, normal to the core plane, and the director **n**. The angle brackets $\langle \ldots \rangle$ denote statistical averaging.

Since the spectral bands of LCs have high values of the molar extinction coefficient [7], the study of the intrinsic electronic absorption spectrum is hampered by the experimental difficulties in obtaining thin films of these crystals. In order to record electronic absorption spectra of the H7T,

an optical cell with a thickness of $d < 1\mu m$ was prepared. This cell was obtained by pressing together two quartz substrates. The polished substrates were cleaned in the followed way: sonicated in hexane, detergent solution, ethanol and distilled water (20 min each time) and then pyrolyzed at 250°C. The uniform homeotropic orientation of the discotic with the optic axis oriented normally to the substrates was obtained by capillary filling the cell in the isotropic phase followed by slow lowering the LC temperature to the operating point. Upon orthoscopic observation by polarized microscope a homeotropic sample presented a black background with irregular individual light point defects against it. The temperature dependence of the spectra of absorption bands were obtained by Hewlett Packard 8452 A diode array spectrophotometer with multiscanning and subsequent averaging. The error in the thermostabilization of the samples was $\pm 0.2^{\circ} C$. In the homeotropic cell the light propagates along the optical axis and the absorption spectra polarized normal to the director **n** were obtained without a polarizer. This experimental geometry also minimizes the depolarizing effect of multiple scattering of light at fluctuations of the director.

RESULTS AND DISCUSSION

The electronic absorption spectra of homeotropically oriented sample of H7T in the discotic Col_{ho} phase at the reduced temperature $\Delta T = T_c - T = 22.5^{\circ} C$ and in isotropic state are shown in Figure 1. T_c is the temperature of the columnar discotic – isotropic phase transition. According to a vibronic progression model [3] the long-wavelength part of the electronic absorption spectrum for the mesogenic triphenylene derivatives consists of several singlet – singlet transitions. The long-wavelength transitions $S_o \rightarrow S_1$ with $\lambda = 358\,nm$ and $S_o \rightarrow S_2$ $\lambda = 332\,nm$ are a forbidden symmetry, whereas $S_o \rightarrow S_3$ and $S_o \rightarrow S_4$ are an allowed symmetry and degenerate. The intensity of the electronic transition $S_o \rightarrow S_3$ with $\lambda = 319\,nm$ is practically independent of the variation of the temperature. The absorption peak of the spectrum ($\lambda_{max} = 270\,nm$) corresponds to the most intense $S_o \rightarrow S_4$ transition. As seen from Figure 1 the peak of the spectrum for Col_{ho} phase is blue-shifted with respect to the isotropic phase, in spite of the resonant dipole – dipole interaction of molecules in a liquid crystal. In general, this interaction leads to the low-frequency shifts of the centers of gravity of the bands in mesophase [8]. The observed blue shift of the absorption maximum can be explained by the existence of strong excitation interactions leading to collective excited states [3]. At the same time, the significant alteration of the electron absorption is possible due to local-field effects in the region of the dense spectrum [9]. Perhaps, in the H7T discotic the mixing of molecular excitations for adjacent

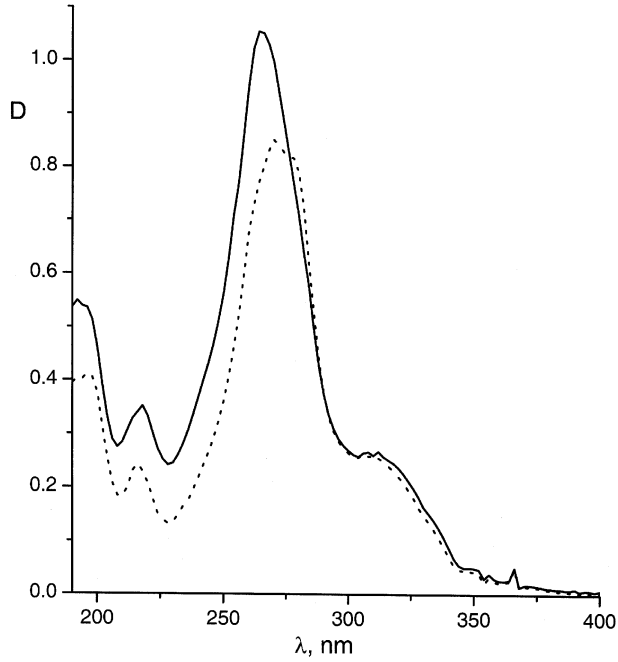

FIGURE 1 Polarized component $D_{\perp}(\lambda)$ of the absorption band of H7T, for a sample with homeotropic orientation (solid curve) at the reduced temperature $\Delta T = 22.5°C$ and in the isotropic phase (dashed curve). Quartz cell, $d < 1\mu m$.

absorption bands caused by the local-field effects is far stronger than the resonant interactions of molecules and that renormalize the spectrum of electronic absorption. The mixing is manifested in the variation of the spectra on passing from the solution to the isotropic LC phase. The resonance interaction between solute molecules and mixing of excitations of these molecules are absent in the solution. Figure 2 shows the normalized spectra of H7T in methylcyclohexane solvent with the concentration 10^{-5} mol/l and in the isotropic phase. One can see from Figure 2 on passing from the solution to the isotropic phase, the maximum of the contour shifts to the blue and the shoulder, corresponding to the $S_o \rightarrow S_3$ transition, shifts to the red. At the same time, the relative intensities and half-widths of the bands have changed. To perform a quantitative comparison, we separated the overlapped bands of the H7T as is in [3]. For this purpose a software Peak-Fit 4.0 is used. Each transition $S_o \rightarrow S_i$ is simulated by the sum of N_k Gaussian bands with the same bandwidth W_k. The amplitude and bandwidth of each Gaussian band are fitting parameters. Since the vibronic progressions are more suitable for the analysis of the solution spectrum,

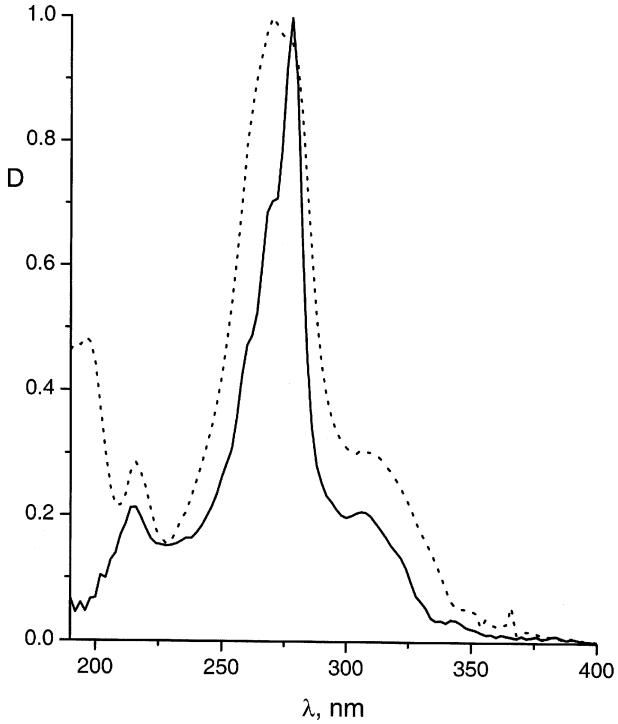

FIGURE 2 Normalized spectra of the diluted H7T solution in methylcyclohexane (quartz cell, concentration $C = 10^{-5}M$, solid curve) and in the isotropic LC (dashed curve).

the fitting was first made on it. Then the spectrum of the isotropic phase of H7T is fitted using the same number of gaussians as that found for the solution. The low-frequency shifts $\Delta\nu_{3,4} = \nu_{3,4}^{sol} - \nu_{3,4}^{iso}$ of gaussians, corresponding to $S_o \rightarrow S_3$ and $S_o \rightarrow S_4$ pure electronic transitions, were $\Delta\nu_3 = 233.8\,\mathrm{cm}^{-1}$ and $\Delta\nu_4 = 97.8\,\mathrm{cm}^{-1}$.

The intensity of the most intense high-frequency S_4 gaussian is pumped out to the low-frequency S_3 gaussian. The proportion of the bandwidths W_3/W_4 decreases from 1.61 to 1.06, on passing from solution to the isotropic phase. Thus, the repulsion of the S_3 and S_4 Gaussian bands, the change of their relative intensities and the equalization of bandwidths are an evidence of the mixing of the corresponding molecular excitations in the isotropic phase caused by resonance dipole-dipole interactions.

At an arbitrary degree of mixing, the dichroic ratio $N = D_\perp/D_i$ of the integrated optical density D_j of all the k bands under the curve can be used for the experimental determination of the parameter [9]

$$S^* = S\sum_k F_k S_{\beta k} / \sum_k F_k \tag{1}$$

from the following formula

$$S^* = 1 - Ng. \tag{2}$$

In Eq. (1), summation is performed over the k bands, F_k are the oscillator strengths of the corresponding transitions, S is the order parameter and the parameter

$$S_{\beta k} = (3\cos^2\beta_k - 1)/2, \tag{3}$$

where β_k is the angle between the transition moment and molecular axis of symmetry **l**. The correction factor g takes into account the anisotropy of the local field of the light wave and has the form

$$g = \frac{\rho_i n_o}{\rho n_i}\left(\frac{f_i}{f_\perp}\right)^2, \tag{4}$$

where ρ and ρ_i are the densities of the LC and isotropic liquid, $n_{o,i}$ are the background ordinary and isotropic phase refractive indices and

$$f_{\perp,i} = 1 + L_{\perp,i}(n_{o,i}^2 - 1) \tag{5}$$

are the background components of the local-field tensor in the absorption band. The parameter $L_\perp$ is a component of the Lorentz tensor **L**, perpendicular to the director. In the isotropic phase $L = 1/3$ and $f_i = (n_i^2 + 2)/3$.

The electronic transitions of the disc-like molecules are polarized within the aromatic plane of the rigid molecular core [10], as is the C-C aromatic stretching vibration previously used in [9] for the measurement of the orientational order parameter S in the LC under consideration. This means that, we have $\beta_k = \beta$ and that the parameter $S^* = SS_\beta$. In this special case the orientational order parameter S of H7T can be calculated from the Eq. (2) taking into account the mixing of molecular excitation. To obtain the background refractive indices at $\lambda = 270$ nm (Fig. 3), we used the experimental values of the refractive indices measured in the region of the wavelengths 488–633 nm [11] and single-band dispersion relation $n_{o,i}^2 = 1 + \lambda^2 A_{\perp,i}/(\lambda^2 - B_{\perp,i})$ [12], where the wavelengths λ are expressed in microns. The fitting parameters A and B depend on the reduced temperature ΔT and on the polarization and the approximation interval of wavelengths. The correction factor g was calculated from (4) with the use of the previously measured values of $L_\perp$ [9] and ρ,ρ_i [13]. In spite of taking into account the local-field effects, we obtained the nonphysical values of the order parameter $S > 1$ from the Eq. (2) by using the integrated optical density D_j of all the k bands under the spectral curve. Since the given curve is formed by a superposition of several vibronic series, we assume that the

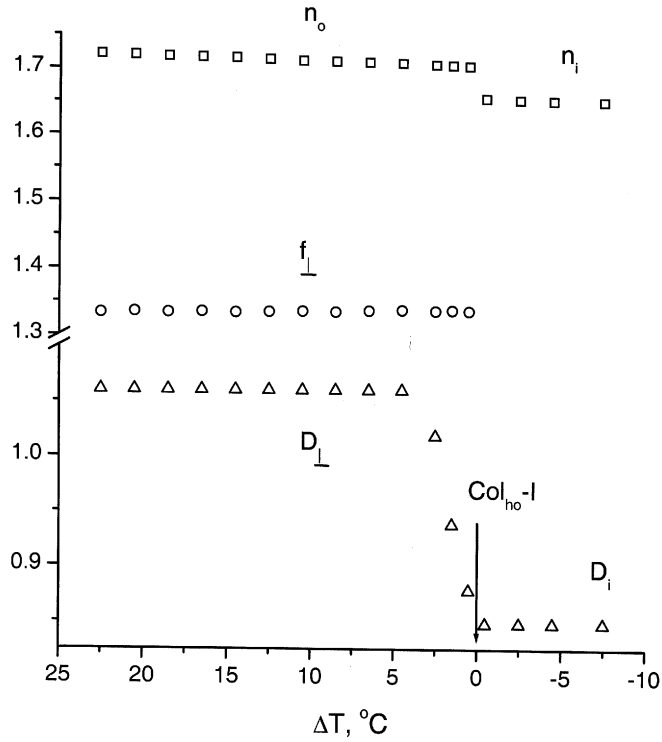

FIGURE 3 Temperature dependencies of the characteristics of H7T in the region of the $S_o \rightarrow S_4$ electronic transition for the background values of the refractive indices ($n_{o,i}$) and the components of the local-field tensor ($f_{\perp,i}$), the optical densities of the sample $D_{\perp,i}(\lambda_{\max})$.

effective values β_k of the vibronic bands are different than that for the pure electronic transitions, i.e. $\beta_k < \pi/2$.

As a rule, in LCs the $n_j(\lambda)$ dispersion is determined by a pair of long-wavelength electronic absorption bands, designated as the λ_1 and λ_2 bands with $\lambda_2 > \lambda_1$ [14]. Apparently, for the H7T these bands λ_1 and λ_2 are associated with the allowed singlet-singlet $S_o \rightarrow S_4$ and $S_o \rightarrow S_3$ long-wavelength transitions. As seen above, $\lambda_1 = 270\,\text{nm}$ band exhibits a strong transition intensity and an absorption anisotropy, and its wavelength sensitive to the phase transition Col_{ho}-I. On the other hand, the transition intensity and absorption anisotropy of the band $\lambda_2 = 319\,\text{nm}$ are all much lower than the λ_1 band, and so its effect on the $n_j(\lambda)$ dispersion can be excluded from the consideration, as a first approximation.

If the orientation of the dipole moment of the transition relative to the molecular axis of symmetry **l** is assigned by the angle β, the relationship

between the experimentally measured optical densities $D_{\perp,i}$ and the corresponding normalized values of the oscillator strength have the form [5]

$$\frac{A_m}{K} = \frac{3n_o D_\perp}{\rho f_\perp^2 (1 - SS_\beta)} \tag{6}$$

$$\frac{A_i}{K} = \frac{3n_i D_i}{\rho_i f_i^2}. \tag{7}$$

Here A_m and A_i are the oscillator strengths of the transition in the mesophase and in the isotropic liquid; $K = \text{const}$, $n_{o,i}$ are the background values of the refractive indices within the absorption band; ρ and ρ_i are the densities of the liquid-crystal and isotropic phases; $f_{\perp,i}$ are the background values of the components of the local-field tensor (5).

The relations (6,7) can be used to estimate the normalized values of the oscillator strength of the $S_o \rightarrow S_4$ pure electronic transition of H7T. For the given transition, the angle $\beta = \pi/2$ and the parameter S_β is equal to $-1/2$. The variability of the $n_{o,i}$ and $f_{\perp,i}$ within the absorption band investigated is small, and the values $D_{\perp,i}$ corresponding to the maximum of the band were used.

As seen from Figure 3 the temperature dependence of the optical density in the Col_{ho} phase does not originate the reduction of the orientational order parameter S with increasing of the temperature, and we obtained the constancy of the parameter $D_\perp$. If the effect of conformational changes of molecules on $D_\perp$ in the Col_{ho} phase is to be excluded, then stronger effects of the mixing on this parameter can be expected. Since the δ correction factor of mixing depends on the temperature [11], these effects can renormalize the behavior of the optical density in the Col_{ho} phase as it is seen in Figure 3. Below $\Delta T = 4^\circ C$ the spectral data is not reliable since an elastic free energy of discotic LCs does not hold strong homeotropic orientation of the sample. An inspection with the microscope confirms the destruction of the perfect orientation at the temperature interval near to the Col_{ho}-I phase transition. The temperature dependence of the oscillator strength $A_{m,i}$ of the H7T discotic transition in the mesophase and in the isotropic liquid are presented in Figure 4. It is seen, that the oscillator strength A_m of the $S_o \rightarrow S_4$ transition of H7T increases abruptly upon the I-Col_{ho} phase transition, and then decreases linearly with the growth of the order parameter S.

The increase of A_m with the growth of the temperature is due to the behavior of $D_\perp$ only, since $f_\perp^2$ is constant, and the temperature dependencies of ρ and n_o have not effect on the curve of the oscillator strength. But, in fact, an absence of the conformational alterations of molecular cores leads to the constancy of A_m within of the mesophase. The constancy of the mean value of the polarizability of H7T molecules in the Col_{ho} phase, which

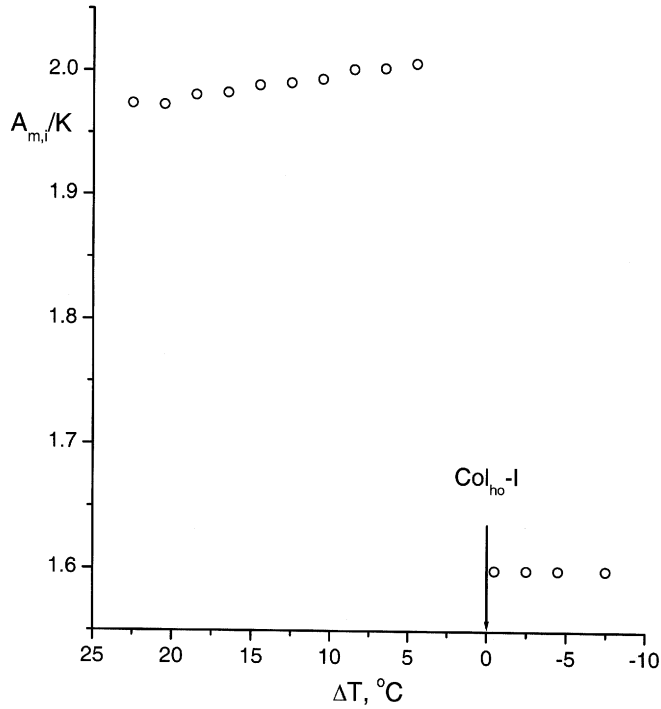

FIGURE 4 Temperature dependence of the normalized oscillator strength $A_{m,i}/K$ of the $S_o \rightarrow S_4$ electronic transition of H7T in the Col_{ho} and the isotropic phase.

was discovered by refraction measurements [11], confirms the constancy of the oscillator strength A_m. Thus, the observed dependence of A_m for $S_o \rightarrow S_4$ transition in the Col_{ho} phase of H7T is caused by the mixing effects only. The variation of the temperature of the isotropic phase of H7T does not result in appreciable changes in the value A_i. The abrupt change in the oscillator strength of the $S_o \rightarrow S_4$ band at the Col_{ho}-I phase transition evidences about changes the π-electron conjugation of the aromatic core of discogenic molecules of H7T. In fact, planes of the outer phenyl rings are not coplanar with each other and with the plane of the central ring, because of the steric effects of hydrogen atoms bonded with aromatic carbon atoms of the molecular core [6]. Since $S_o \rightarrow S_4$ transition is polarized in plane of the aromatic core, we assume that the observed break of the oscillator strength at Col_{ho}-I transition is due to the conformational alterations of the coplanarity of the phenyl rings. The inequality $A_m > A_i$ means the reduction of the angles between outer and central phenyl rings at the transition from the isotropic liquid to the columnar phase.

Translational ordering of the discogenic molecules in Col_{ho} phase leads to higher planarity of the central cores, and consequently, to the increase of the π-electron conjugation of the aromatic core. Thus, the difference between mean values of the effective polarizability $\bar{\gamma}$, of about 6 Å in the columnar and isotropic phases [11], is caused not only by the features of the local-field effects in these phases, but also by the alteration of the conformation of discogenic molecular cores at Col_{ho}-I transition.

CONCLUSION

Nonphysical values of the absolute parameter order S of H7T, calculated from the measurements of the dichroic ratio $D_{\perp}/D_i$ in the region of the dense electronic spectrum, evidenced a nonhomogeneous polarization of the vibronic gaussians series of the long-wave electronic transitions, under consideration. In order to ascertain the orientation of the vibronic transitions, located out of the plane of the molecular cores, further spectral investigations are needed. The analysis of the spectrum showed that a mixing of electronic excitations appears in discotics and it renormalizes the temperature behavior of the measured values of the optical density and the oscillator strength of the electronic absorption bands. For the first time, it was observed that a translational ordering of the discogenic molecules in the Col_{ho} phase of H7T leads to a conformational state of molecular cores with more planarity than in the isotropic phase. Finally, the applied approaches indicated the efficiency of the electronic absorption spectroscopy for conformational analysis of the discotic LCs.

REFERENCES

[1] Chandrasekhar, S., & Krishna Prasad, S. (1999). *Contemp. Phys.*, *40*, 237.
[2] Aver'yanov, E. M. (1997). *J. Struct. Chem.*, *35*, 71.
[3] Marguet, S., Markovitsi, D., Millie, P., Sigal H., & Kumar, S. (1998). *J. Phys. Chem. B*, *102*, 4697.
[4] Markovitsi, D., Bengs, H., & Ringsdorf, H. (1992). *J. Chem. Soc. Faraday Trans.*, *88*(9), 1275.
[5] Aver'yanov, E. M. & Mineev, L. I. (1986). *J. Struct. Chem.*, *27*, 245.
[6] Ferraris, G., Jones, D. W., & Yerkess, J. (1973). *Zeitschr. Fur Kristallogr.*, *138*, 113.
[7] Blinov, L. M. (1983). *Electro-Optical and Magneto-Optical Properties of Liquid Crystals*, Wiley: New York.
[8] Aver'yanov, E. M. (1980). *Sov. Phys. Solid State*, *22*(6), 1088.
[9] Aver'yanov, E. M., Gunyakov, V. A., Korets, A. Y., & Akopova, O. B. (2000). *Opt. Spectrosc.*, *88*, 891.
[10] Uznanski, P., Marguet, S., Markovitsi, D., Schuhmacher, P., & Ringsdorf, H. (1997). *Mol. Cryst. Liq. Cryst.*, *293*, 123.
[11] Gunyakov, V. A. & Shibli, S. M. (2002). *Liq. Cryst.*, *29*, (in the press).

[12] Wu, S. T. (1991). *J. Appl. Phys.*, *69*(4), 2080.
[13] Gunyakov, V. A., Shestakov, N. P., & Shibli, S. M. Submitted in Liq. Cryst.
[14] Khoo, I. C. & Wu, S. T. (1993). Optics and Nonlinear Optics of Liquid Crystal. World Scientific: London.