

Experimental solution of the local-field problem in discotic liquid crystals

E. M. Aver'yanov^{*}) and V. A. Gunyakov

L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

A. Ya. Korets

Krasnoyarsk State Technical University, 660036 Krasnoyarsk, Russia

O. B. Akopova

Ivanovo State University, 153025 Ivanovo, Russia

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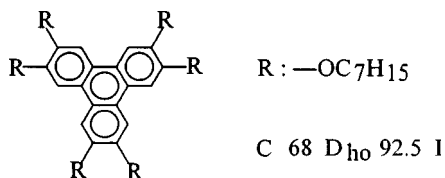
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Polarized light-absorption spectra are obtained for single-domain planar-oriented samples of the discotic D_{ho} . Previously predicted spectral effects induced by resonant dipole–dipole interactions of the molecules are observed. New methods for determining the parameters of the local field in the D_{ho} phase are developed which take into account the mixing of the molecular excitations. It is shown that the two-dimensional crystalline ordering of the molecular columns decreases the anisotropy of the local field for this phase. © 1999 American Institute of Physics. [S0021-3640(99)00613-1]

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1. Experimental data on the anisotropy of the local electric field in liquid crystals (LCs) with disk-shaped molecules are important for analyzing a variety of questions which are being actively discussed: the possibility of a ferroelectric state in discoidal nematics N_D (Refs. 1 and 2), the polarity of molecular columns and their antiferroelectric ordering in the discotics $D_{h(0,d)}$ (Refs. 3 and 4) the quasi-one-dimensional electric and photoelectric conductivity of the $D_{h(0,d)}$ phases,⁵ the qualitative difference of the characteristic features in the polarized absorption spectra of calamitic and discoidal LCs,⁶ and the effect of two-dimensional crystalline ordering of columns on the anisotropy of the dipole–dipole interaction of the molecules. However, such data have been lacking thus far. To determine the local-field parameters in discotics by spectral methods⁷ these methods needed to be modified to take into account the mixing of molecular excitations,⁸ and single-domain planar-oriented samples needed to be obtained for polarized spectral investigations. These problems are solved in the present work.

2. The object of investigation was the discotic liquid crystal THE7 with the indicated temperatures (°C) of the phase transitions between crystal, discotic D_{ho} , and isotropic liquid ($C-D_{ho}-I$).



The uniaxial phase of D_{ho} is a two-dimensional hexagonal lattice of molecular columns, which are perpendicular to this lattice and parallel to the director \mathbf{n} .⁵ The molecular cores are translationally ordered along the axes of the columns. The orientational order of the molecular axes \mathbf{l} (perpendicular to the plane of the core) relative to \mathbf{n} is characterized by the order parameter $S = \langle 3 \cos^2 \theta_{ln} - 1 \rangle / 2$.

Single-domain films of the discotic D_{ho} with an area of several square centimeters, thickness $d = 10\text{--}20 \mu\text{m}$, and uniform orientation of \mathbf{n} parallel to the substrates were obtained in NaCl, KBr, CaF₂, and Ge cells using a modification of the method of Ref. 9. Polished substrates were cleaned by conventional chemical methods without using surfactants. The initial uniform homeotropic orientation of the LCs with the optic axis normal to the substrates was obtained by capillary filling of the cell in the isotropic phase followed by slow cooling and lowering of the temperature of the LC to the working range. Next, for a monitored plane-parallel arrangement of the substrates and fixed d , unidirectional stepped displacements of one substrate relative to the other were performed in 15-min intervals using a micrometric screw, with visual and spectral monitoring of the orientation of the sample at the end of each interval. Spectral monitoring consisted of measuring the dependence $D_e(\nu_k, l)$ of the optical density of the IR absorption bands for the extraordinary light wave, polarized in the \mathbf{Ns} plane, as a function of the shift l of the substrate. Here \mathbf{N} is the normal to the cell surface and is parallel to the direction of propagation of the light wave, and \mathbf{s} is the direction of the relative displacement of the substrates. The dependences $D_e(\nu_k, l)$ are presented in Fig. 1 for a number of absorption bands. Saturation of these dependences, which corresponds to a planar orientation of the director \mathbf{n} and the equality $D_e(\nu_k, l_c) = D_{\parallel}(\nu_k)$, is observed for $l_c \approx 50d$. For orthoscopic observation in crossed prisms, such a sample with an area of several square centimeters is a uniformly colored domain, a fragment of which is displayed in Fig. 2. For an ordinary light wave polarized in a direction normal to the plane \mathbf{Ns} , the position and optical density $D_{\perp}(\nu_k, l)$ of the IR absorption bands do not change in the process of orienting the LC and are identical to those for the initial homeotropic and final planar orientations. This is illustrated in Fig. 3. The spectra were obtained on an automated Specord M82-57 spectrophotometer with multiscanning and subsequent averaging.

For $d = 10\text{--}20 \mu\text{m}$ the planar orientation of the discotic remains stable for many hours. As d decreases or the temperature approaches the $D_{ho}\text{--}I$ transition temperature, the relaxation time of the planar-oriented sample in an unoriented state decreases rapidly. With increasing $d > 20 \mu\text{m}$, the uniformity of the initial homeotropic sample and of the planar-oriented sample obtained from it degrades. The results presented below are for temperature $\Delta T = T_{ID} - T = 22.3 \text{ K}$, far from the $D_{ho}\text{--}I$ transition.

3. The displacement of the maxima ν_{mj} of the IR absorption bands of the LC, polarized parallel ($j = \parallel$) and perpendicular ($j = \perp$) to the director, relative to their positions ν_{mi} in the isotropic phase is determined by the order parameter S of the molecules, the anisotropy $\tau = (L_{\parallel} - L_{\perp})/3$ of the Lorentz tensor \mathbf{L} of the LC, and the angle β

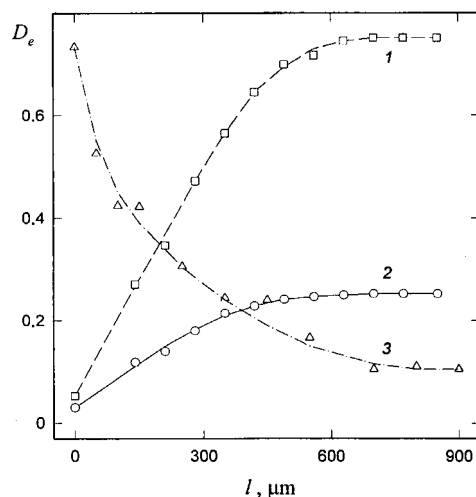


FIG. 1. Optical density $D_e(\nu)$ of the LC THE7 at $T=70.2^\circ$ for the extraordinary light wave as a function of the relative shift l of the substrates for $\nu=830$ and 865 cm^{-1} (1 and 2, KBr cell, $d=12.4\ \mu\text{m}$) and $\nu=1616\text{ cm}^{-1}$ (3, CaF_2 cell, $d=17.6\ \mu\text{m}$). The curves are interpolations.

between the transition dipole moment \mathbf{d} and the molecular axis \mathbf{I} . For all isolated absorption bands of THE7 the expected inequality $\nu_{m\perp} > \nu_{mi}$ is satisfied⁶ irrespective of the value of β . The bands presented in Fig. 4, $\nu_{mi}^{(1)}=780$, $\nu_{mi}^{(2)}=811$, $\nu_{mi}^{(3)}=836$, $\nu_{mi}^{(4)}=869.5$, and $\nu_{mi}^{(5)}=908\text{ cm}^{-1}$, are characterized by different values of β , where for the strongest bands $\beta_2 > 54.7^\circ > \beta_4 > \beta_3 \approx 0$. These inequalities correspond to the ratios

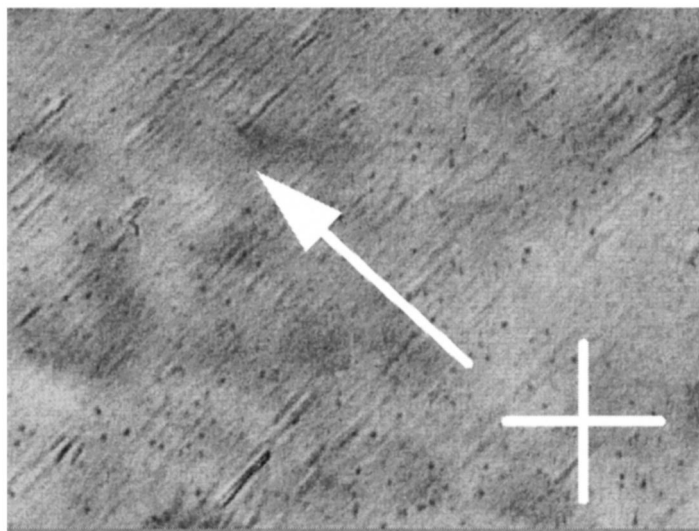


FIG. 2. Texture of the planar-oriented discotic THE7 in crossed prisms, indicated by the cross. The arrow shows the direction of the relative shift of the substrates $\mathbf{s} \parallel \mathbf{n}$.

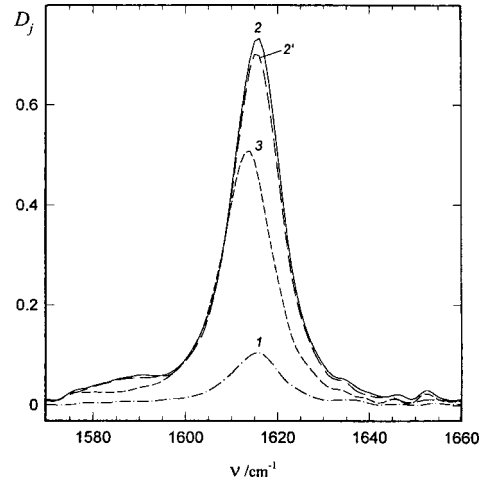


FIG. 3. Polarized components $D_j(\nu)$ of the absorption band of the LC THE7 with $j = \parallel$ (1), \perp (2, 2') for a sample with planar (1, 2) and homeotropic (2') orientation and in the isotropic phase (3, CaF₂ cell, $d = 17.6 \mu\text{m}$).

$\nu_{mi}^{(n)} > \nu_{m\parallel}^{(n)}$ for $n = 2-4$ and $\Delta\nu^{(3)} > \Delta\nu^{(4)}$, which are expected for a discoidal LC.⁶ Here $\Delta\nu^{(n)} = \nu_{mi}^{(n)} - \nu_{m\parallel}^{(n)}$. The values $\Delta\nu^{(3)} = 6.6$ and $\Delta\nu^{(4)} = 4.2 \text{ cm}^{-1}$ demonstrate the first reliable observation of the splitting of polarized intrinsic absorption bands of a LC as a result of resonant dipole-dipole intermolecular interactions. This splitting is similar in nature to the Davydov splitting of polarized excitonic-absorption bands in molecular crystals.^{7,10} High values of S and low values of β in discoidal LCs is optimal for observing this effect in uniaxial LCs,⁶ as the present experiment confirms.

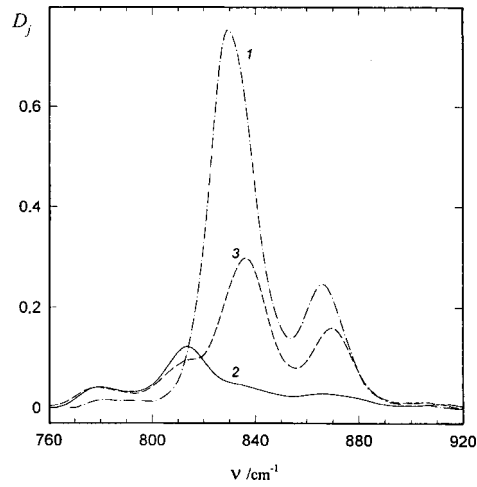


FIG. 4. Polarized components $D_j(\nu)$ of the absorption bands of the LC THE7 (KBr cell, $d = 12.4 \mu\text{m}$). The labels are the same as in Fig. 3.

It is seen in Fig. 3 that another unusual relation $\nu_{m\parallel} = \nu_{m\perp} > \nu_{mi}$, possible in discoidal LCs for $\beta \leq 90^\circ$ and high values of S and τ ,⁶ is satisfied. The absorption band $\nu_{mi}^{(6)} = 1613.5 \text{ cm}^{-1}$ corresponds to vibrations of the molecular core of THE7 with $\beta \approx 90^\circ$ and is optimal for observing this effect; in addition, the inequality $\Delta\nu^{(3)} \approx |\Delta\nu^{(6)}|$ agrees with expectations.⁶

Thus, polarized absorption of a planar-oriented discotic D_{ho} demonstrates some highly characteristic spectral features which qualitatively distinguish uniaxial discoidal LCs from uniaxial calamitic LCs (formed by rod-shaped molecules) and are due to the difference of the local symmetry of these objects.⁶ The relations $\nu_{m\perp} > \nu_{mi} > \nu_{m\parallel}$ and $\nu_{mj} > \nu_{mi}$ observed for the two-dimensional crystal D_{ho} correct the widely held belief that the absorption bands undergo a “red” Lorentz shift when the liquid crystallizes.

4. The isolated group of bands $\nu^{(1)} - \nu^{(5)}$ noted above and the band $\nu^{(6)}$ were used to determine the components L_j . The transition from a dilute solution of THE7 in CCl_4 to the isotropic phase of the LC is accompanied by a low-frequency shift of the bands $\nu^{(1)} - \nu^{(5)}$ and by a change in their relative intensities and half-widths. This attests to the presence of mixing of the corresponding molecular vibrations in the LC as a result of local-field effects.⁸ With this mixing taken into account, the components L_j can be found from the system of equations⁸

$$\text{Tr} \mathbf{L} = 1, \quad N_2 g_2 (N_1 g_1 + 2) = 3, \quad (1)$$

where $N_1 = D_{\parallel} / D_{\perp}$ and $N_2 = D_{\perp} / D_i$ are the dichroic ratios of the integrated optical densities D_j of the entire group of bands $\nu^{(1)} - \nu^{(5)}$,

$$g_1 = \frac{n_{b\parallel} \left(\frac{f_{b\perp}}{f_{b\parallel}} \right)^2}{n_{b\perp} \left(\frac{f_{b\parallel}}{f_{b\perp}} \right)^2}, \quad g_2 = \frac{\rho_i n_{b\perp} \left(\frac{f_{bi}}{f_{b\perp}} \right)^2}{\rho n_{bi} \left(\frac{f_{b\perp}}{f_{bi}} \right)^2}, \quad (2)$$

n_{bj} are the background refractive indices for the group of bands under study, $f_{bj} = 1 + L_j (n_{bj}^2 - 1)$ are the background components of the local-field tensor f_b , and ρ and ρ_i are the densities of the liquid-crystal and isotropic phases. The values $n_{b\parallel} = 1.452$, $n_{b\perp} = 1.527$ ($\Delta T = 22.3 \text{ K}$) and $n_{bi} = 1.487$ ($\Delta T = -10 \text{ K}$) were measured in the transmission region of the LC, $\nu = 1900 - 2500 \text{ cm}^{-1}$, by an interference method using a Ge cell. The ratio $\rho / \rho_i = 1.026$ was measured for the same values of ΔT . The parameters in system (1) are $L_{\parallel} = 0.679$, $L_{\perp} = 0.161$, $g_1 = 0.457$, and $g_2 = 1.338$.

The components L_j for the band $\nu^{(6)}$ were determined by three different methods. The first method uses the system of equations (1) with the parameters $N_1^* = \delta_1 N_1$ and $N_2^* = \delta_2 N_2$, where the corrections⁸

$$\delta_1 = \frac{1 + D_{\parallel}^{(7)} / D_{\parallel}^{(6)}}{1 + D_{\perp}^{(7)} / D_{\perp}^{(6)}} \quad \text{and} \quad \delta_2 = \frac{1 + D_{\perp}^{(7)} / D_{\perp}^{(6)}}{1 + D_i^{(7)} / D_i^{(6)}} \quad (3)$$

take into account the mixing of the $\nu^{(6)}$ band with the intense $\nu_{mi}^{(7)} = 1507 \text{ cm}^{-1}$ band, for which $\beta_7 = \beta_6$. The values $\delta_1 \approx 1$ and $\delta_2 = 0.8$ were obtained for the experimental conditions corresponding to Fig. 3. Using these parameters in Eq. (1) gives the following values: $L_{\parallel} = 0.642$, $L_{\perp} = 0.179$, $g_1 = 0.498$, $g_2 = 1.285$, and $SS_{\beta} = -0.447$. For $\beta_6 = 90^\circ$ we obtain hence $S = 0.894$ and $\tau_0 = \tau(S = 1) = 0.173$.

The local-field parameters presented above are very sensitive to the mixing of the bands $\nu^{(6)}$ and $\nu^{(7)}$. The approximation $\delta_{1,2} = 1$ gives almost isotropic values

$L_{\parallel}=0.391$, $L_{\perp}=0.305$, $g_1=0.915$, and $g_2=0.997$ and strongly underestimated values $S=0.809$ and $\tau_0=0.035$. The latter two values correspond to the inequalities $\nu_{m\parallel}^{(6)} > \nu_{mi}^{(6)} > \nu_{m\perp}^{(6)}$ (Ref. 6), which contradict Fig. 3.

The second method of determining the components L_j uses the equality $\nu_{m\parallel} = \nu_{m\perp}$, which is equivalent to the equation⁶

$$N_1^* \frac{n_{b\perp} f_{b\perp}}{n_{b\parallel} f_{b\parallel}} = \frac{L_{\perp}(3n_{b\perp}^2 + 1) - 1}{L_{\parallel}(3n_{b\parallel}^2 + 1) - 1} \quad (4)$$

or

$$\frac{n_{b\perp}^2 f_{b\parallel}(3 - 2N_2^* g_2)}{n_{b\parallel}^2 f_{b\perp} N_2^* g_2} = \frac{L_{\perp}(3n_{b\perp}^2 + 1) - 1}{L_{\parallel}(3n_{b\parallel}^2 + 1) - 1}, \quad (5)$$

since equating the left-hand sides of Eqs. (4) and (5) gives the second of Eqs. (1). The condition $\text{Tr } \mathbf{L}=1$, taken together with Eq. (4), gives $L_{\parallel}=0.645$, $L_{\perp}=0.177$, $g_1=0.495$, $g_2=1.290$, $SS_{\beta}=(N_1^* g_1 - 1)/(N_1^* g_1 + 2) = -0.447$, and $\tau_0=0.175$. Replacing Eq. (4) with Eq. (5) gives close values: $L_{\parallel}=0.640$, $L_{\perp}=0.180$, $g_1=0.501$, $g_2=1.282$, $SS_{\beta}=1 - N_2^* g_2 = -0.444$, and $\tau_0=0.173$. In the approximation $N_2^*=N_2$ the system of equations comprising the relation $\text{Tr } \mathbf{L}=1$ and Eq. (5) has no physical roots L_j , which likewise signifies the need to take into account the mixing of the bands $\nu^{(6)}$ and $\nu^{(7)}$.

The third method of determining the components L_j is to use the second equation from Eqs. (1) and Eq. (4) or (5), which makes it possible to avoid the *a priori* assumption that $\text{Tr } \mathbf{L}=1$. The results are $L_{\parallel}=0.663$, $L_{\perp}=0.179$, $\text{Tr } \mathbf{L}=1.021$, $g_1=0.485$, $g_2=1.285$, $S=0.894$, and $\tau_0=0.180$. Thus one finds that the condition $\text{Tr } \mathbf{L}=1$ holds within the limits of experimental accuracy; this has been a matter of dispute in the molecular-statistical theory.⁷

5. The results presented above, which were obtained on planar-oriented samples in cells consisting of different materials and by different methods and for different groups of bands give nearly the same values: $L_{\parallel}=0.66 \pm 0.02$, $L_{\perp}=0.17 \pm 0.01$, $g_1=0.48 \pm 0.02$, and $g_2=1.31 \pm 0.03$. The quantity $S=0.890 \pm 0.004$ agrees with the NMR data $S=0.88 \pm 0.92$ (Refs. 5 and 11) for the homolog THE6 for the same value of ΔT . The ratio of the components $f_{b\parallel}=1.73$ and $f_{b\perp}=1.23$ of the local-field tensor corresponds to a higher electric conductivity of the discotic D_{ho} along the columns⁵ and is opposite to the ratio of these components in uniaxial calamitic LCs.⁷ The experimental value $\tau_0=0.18 \pm 0.01$ is greater than the estimated values of this parameter¹ which admit the possibility of a polar phase of the discoidal nematic, and it lowers the corresponding minimum required value of the constant molecular dipole moment along the \mathbf{I} axis. However, the value of τ_0 obtained is less than the theoretical value $\tau_0^*=0.227$ calculated for THE7 using Eq. (4) of Ref. 12, with allowance for the orientational ordering of the molecules and the experimental values¹³ of the column diameter $2a_l=21.94 \text{ \AA}$ and the intermolecular distance in the column $2a_l=3.59 \text{ \AA}$. Since the value of τ_0^* neglects the translational ordering of the molecules in the columns and the two-dimensional ordering of the columns themselves, the relation $\tau_0^* > \tau_0$ indicates that the anisotropy of the tensor \mathbf{L} is lower in the D_{ho} phase on account of the difference of the discotic and nematic ordering of the molecules.

The method proposed here for obtaining and monitoring planar-oriented samples of a discotic LCs greatly expands the possibilities of investigating the structure and properties of these objects by polarized absorption spectroscopy, Raman scattering, and luminescence methods.

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*¹e-mail: aver@iph.krasnoyarsk.su

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