

Spectral and thresholds lasing characteristics of the dye doped steroid cholesteric liquid crystals

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Absorption spectra, fluorescence spectra and quantum yields of dyes of various classes in cholesteric liquid crystals (CLC) and in isotropic solutions as well as the thresholds of their lasing in CLC were investigated. The increase of quantum yields of dyes in concentrated CLC-solution in comparison with diluted isotropic ones are established for the first time. It has been shown that neutral phenolone dyes with voluminous terminal groups which hinder aggregation of their molecules in concentrated solutions.

I. INTRODUCTION

One of the types of lasers with distributed feedback (DFB) on static periodical structures with DFB is the laser on the base of cholesteric liquid crystals (CLC) activated with lasing dyes. This laser was for a first time realized in [1]. In the planar texture of oriented CLC, DFB is caused by Bragg scattering of light on the natural grating formed by helical structure of orientation of layers of CLC (phase grating), as well as on the amplitude grating which arises due to partial ordering of the dye in the liquid crystal. One-dimensional periodicity of the refractive index in the planar texture is oriented perpendicularly to the surfaces which confine the layer, i.e., along the axis of the helical structure of CLC. The period of modulation of the refractive index (period of phase grating), as well as of that of amplitude grating, by virtue of central symmetry of macroscopically ordered layer, is equal to one-half of the helical pitch P . The helical structure of CLC doped with lasing dye causes high degree of integration of the DFB laser on its basis, because main elements of laser, namely, active medium, resonator and tunable selector are combined in the thick of the layer of liquid crystal.

In the first time, the frequency tuning in the DFB lasers on the basis of doped CLC was realized by means of temperature changes of the helical pitch [1]. At thickness of the CLC layers equal to several tens micrometers which are necessary for operation of the laser and for orientation of the layer by rubbing of the substrates and their shift [2], there realizes weak binding of CLC with orientating substrate. At such a binding, change of the helical pitch of CLC proceeds continuously and monotonously, in contrast with the case of strong binding where P changes jump wise [3]. Constructively, the DFB laser on the basis of CLC consists of thin layer of planar texture doped with lasing dye. The texture is formed with the use of substrates which determine the orientation of the molecules of liquid crystal on their profiled surface. As the source of excitation in such a laser, one uses coherent radiation of another laser, so its can be regarded as accessory converter of laser radiation. The duration of excitation pulses in this case must be < 100 ns to avoid destruction of the planar texture with high-power exciting radiation. For viscous CLC on the basis of mixtures of cholesterol derivatives, planar texture which is formed by substrates retains its high quality only below 60-70 μm thickness, for this reason a feature of such lasers is great angular divergence of radiation [4]. Evident simplicity of the construction and the possibility of continuous tuning of frequency of lasing gives the perspective of the use of such a laser in the spheres where one needs first of all cheap, simple and compact frequency tunable sources of coherent radiation.

Lasing in dye-doped CLC- based laser detailed was studied in the mixture of steroid cholesterol derivatives which are neutral and no polar solvents. This restricts the choice of activating doping dyes with primarily neutral molecules [5]. In such materials, the lasing of DFB- laser on the basis of CLC was obtained in the 580-610 nm region with the use of two dyes, analogues of 3-aminobenzanthrone, with low efficiency of lasing [2]. For expanding of the region of tuning and for increasing of the efficiency of lasing of such a laser, it is necessary to investigate the spectral features of the dyes which show lasing in CLC, as well as the conditions of lasing of the dyes of other classes in such media. The study of the characteristics of lasing of DFB laser on steroid CLC have shown that the energy output of such a laser is limited due to strong coupling of the waves in CLC directed in opposite directions; there exists, however, a possibility to increase it due to induced thermal phase grating [6].

Since the dye-doped CLC - based lasers are single in world by type of lasers, active media in which possible realize in the form of surfaces, in principle, any areas and curvatures, in the absence of mirror resonator, in the last years they cause the big interest for development of displays to increased brightness or color projection screens [7]. Begin active studies of such lasers on base new, more technological than viscous of cholesterol derivatives, CLC-materials [8-10].

In this paper we present the investigations of the spectral properties of doped steroid CLC and threshold characteristics of their lasing .

II. EXPERIMENTAL TECHNIQUE

The experiments were performed on the laser setup similar to that described in [6]. A DFB laser was pumped by the second harmonic of a Nd³⁺ laser ($\lambda=530$ nm) with passive Q-switch oscillating in a single pulse mode. The features of the laser setup and the details of the techniques of measurements are described in [6]. The error in measuring of threshold excitation intensities was 10%, and in measuring of the energy of lasing, 20%. As CLC, in the most part of the experiments we used the base mixture of cholesterol derivatives with the following composition: 40% cholesteryl oleate, 25% cholesteryl chloride, and 35% cholesteryl pelargonate. In the case of necessity of positioning of the selective reflection (SR) bands in arbitrary region of the contour of the dye fluorescence, we varied the ratio of the components of this mixture. The planar texture of CLC doped with dye (active element of DFB laser) was formed between glass substrates with SnO₂ layer, over which there was the layer of polyamide lacquer (PAL) with thickness <1 μ m rubbed in one direction. The thickness of the layer was controlled by teflon spacers. The technique of producing of samples of doped CLC, active elements of DFB laser, with high-quality planar texture of liquid crystal, is described in [4,6].

We used dyes of type «for QE» synthesized in the Institute of Organic Chemistry of the Ukrainian Academy of Sciences (ketocyanine dyes) and Organic Intermediates & Dyes Institute (OI&DI), Moscow, Russia (phenolone dyes) without additional purification. Quantum yield of the dyes in CLC was measured with relative method with the use of the etalon solution rhodamine 6G in ethanol; the error of the measurement was 20%. When studying the characteristics of lasing, the concentration of dyes was 0.3- 0.5 mass %. Transmittance and fluorescence spectra of the doped CLC were recorded by a spectrophotometer SF-20 and a spectrometer «Hitachi» MPF-4, respectively.

III. RESULTS AND DISCUSSION

Main requirements to the dyes used for activation of CLC are high efficiency of lasing and good solubility in this matrix for ensuring full absorption of the pumping radiation in the layers with thickness of several tens of micrometers. Also necessary are high quantum yields of fluorescence in such solutions for ensuring low thresholds of lasing of the DFB laser. Up to now, no clear criteria are found for the choice of the dye as lasing dopant to CLC. Such characteristics as the solubility of the dye can be determined mainly experimentally, starting from the present data on nematics. Determining role in dissolving in nematics, according to [11-12], plays the correspondence between the spatial structures of dopant and nematic molecules, as well as the donor-acceptor properties of the nematics as a solvent. As well as the mixture of steroid CLC are neutral and weakly polar solvents, the dyes which in solutions dissociate with formation of ions at high concentrations in thin films probably are present in the form of aggregates.

During testing of rhodamine 6G, one of the most efficient laser dyes, in the used mixture of CLC, signs of aggregation appeared at as low mass concentrations as 0.001% in the isotropic solution, i.e., above the phase transition temperature. As one can see in Fig.1 (curve 1), at this concentration in the absorption spectrum short-wave maximum appears which is 30 nm shifted with respect to the maximum of absorption of the main form ($\lambda = 530$ nm). With the increase of the dye concentration in the planar texture of oriented CLC, the relative intensity of the short-wave maximum increases and, at concentration of ca. 0.1% becomes greater than the intensity of absorption in the main form of the dye (Fig. 1, curve 2). The maximum at 580 nm in this spectrum is caused by the SR of the planar texture of CLC. As it is known [13], such features in the absorption spectra are characteristic for associated forms of dyes. Strong association at room temperature which was accompanied by the more than one order decrease of the quantum yield as compared with diluted ethanol solutions (Table 1 and 2) hindered the use of rhodamine 6G, including its salts with various anions, Nil blue and ionic polymethine dyes as dopants to the used mixture of CLC. No lasing with these dyes was obtained in all range of intensities of excitation up to the thermal destruction of the planar texture [6]. In this connection, the use of rhodamine 6G in some experiments [14-15] with lasing in cholesteryl pelargonate can be explained by essentially smaller degree of aggregation of the dye molecules in the range of existence of its cholesteric mesophase (79-90°C). Due to the heating of the dye up to such temperatures, the increase of the quantum yield of fluorescence caused by the decrease of the amount of aggregates compensates its temperature decrease, which gives the possibility to obtain lasing in the conditions of resonator with high "Q" (in the absence of distributed feedback).

Neutral polymethine dyes, ketocyanines (No 2 and 3 in Table 1), which show efficient lasing in ethanol solutions [16], easily dissolve in the used mixture of CLC, and at concentration below 0.1% they did not show characteristic signs of association. However, in contrast with ethanol solutions, in CLC the structure of the absorption bands appear which is typical for non-polar solutions of ketocyanines (Fig.2, curve 1), and phototropic transformations in CLC are pronounced to still greater extent. Even in the process of recording of the absorption spectrum on the spectrophotometer (during repeated recording 3-5 minutes later), the integral intensity of the absorption band decreases (Fig. 2, curve 2). The phototropic transformation of the stereo isomers of the ketocyanine dyes 411 and 3240_u in the used mixture of CLC was manifested also in the fluorescence spectra. The photochemical instability of ketocyanines in CLC is connected with trans-cis isomerization of its molecule, and low quantum yield of fluorescence (see Table 2) hinder their use as lasing admixture to CLC. Such solutions underwent complete decolourisation after irradiation with even a single pulse of laser pumping with 5 MW·cm⁻² intensity.

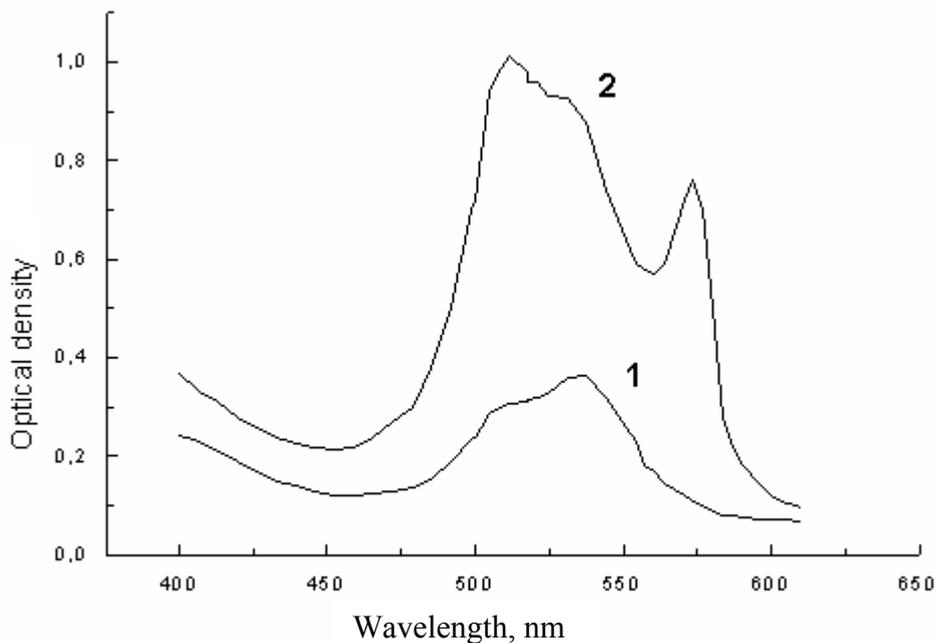


Fig. 1: Absorption spectrum of rhodamine 6G in isotropic CLC (1) at 42°C . Layer thickness 5 mm. Concentration 0.001%. Absorption spectrum of the same dye in oriented CLC (2). Layer thickness 50 μm, concentration 0.1%.

Table 1: Spectroscopic characteristics of dyes in the ethanol solutions

No	Name	$\lambda_{\text{max. abs.}}$, nm	$\lambda_{\text{max. fluor.}}$, nm	Quantum yield, %
1	rhodamine 6G	530	560	95
2	411	540	590	40
3	3240 _u	530	-	-
4	F 444	552	598	66
5	F 439	568	605	39
6	F 427	550	594	42
7	F 490	560	602	45
8	3- diethylaminobenzanthrone	528	660	-

Notice. Concentration of dyes - 0,001 mass %, layer thickness - 5 mm.

In analogy with the dye 3-diethylaminobenzanthrone (No 8 in Tables 1 and 2), for which lasing of DFB laser on the basis of CLC was obtained for a first time [1], we used, for activation of liquid crystals, also neutral dyes of phenolone series whose spatial structure is close to the structure of the dye No 8 (see Table 2) [17]. It is essential that phenolone dyes have high photo stability in neutral media to which CLC belong. In addition, the lasing

efficiency of such dyes is considerably higher than for analogues of 3-aminobenzanthrone.

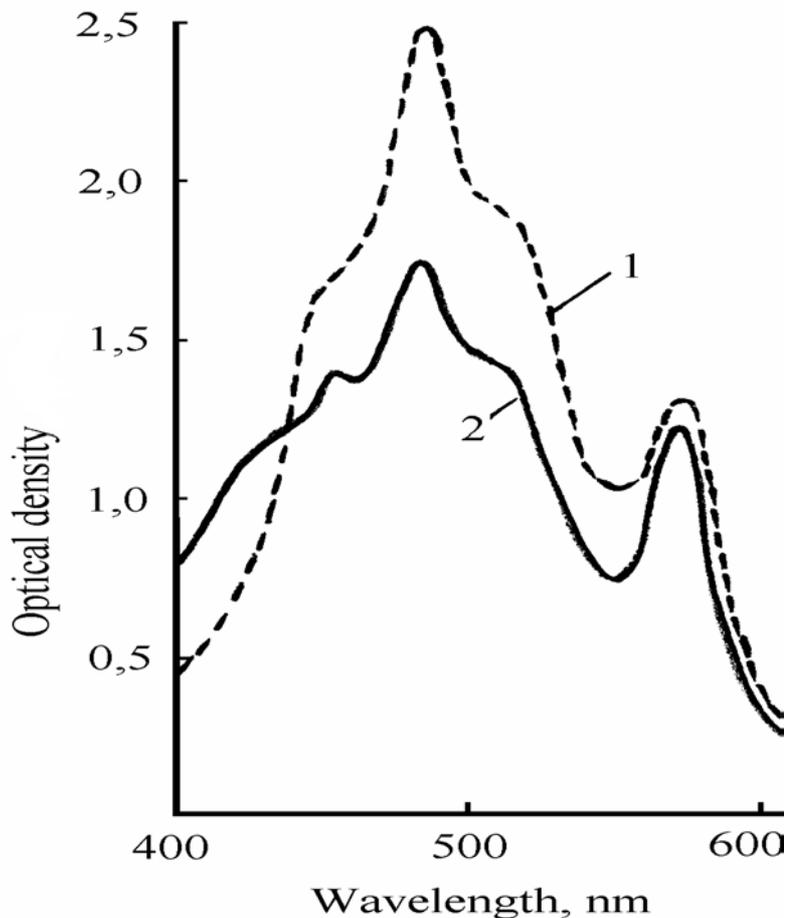


Fig.2: Absorption spectrum of dye No 411 in oriented CLC: 1- original spectrum, 2 – spectrum at repeated recording (3-5 min. after irradiation). Concentration 0,13%

Table 2: Spectroscopic characteristics and threshold intensity excitation of dyes in oriented CLC

No	Name	$\lambda_{max.}$ abs., nm	$\lambda_{max.}$ fluor., nm	Quantum yield, %	$I_{thr.}$ kW / cm ⁻²
1	rhodamine 6 G	540	600	6	-
2	411	495	545	2	-
3	3240 _u	490	540	1,5	-
4	F 444	515	570	21	-
5	F 439	494	583	18	-
6	F 427	536	566	84	64
7	F 490	530	595	61	70
8	3-diethyl aminobenzanthrone	500	595	57	80

Notice. Concentration of dyes - 0,1 mass %, layer thickness - 50 μ m.

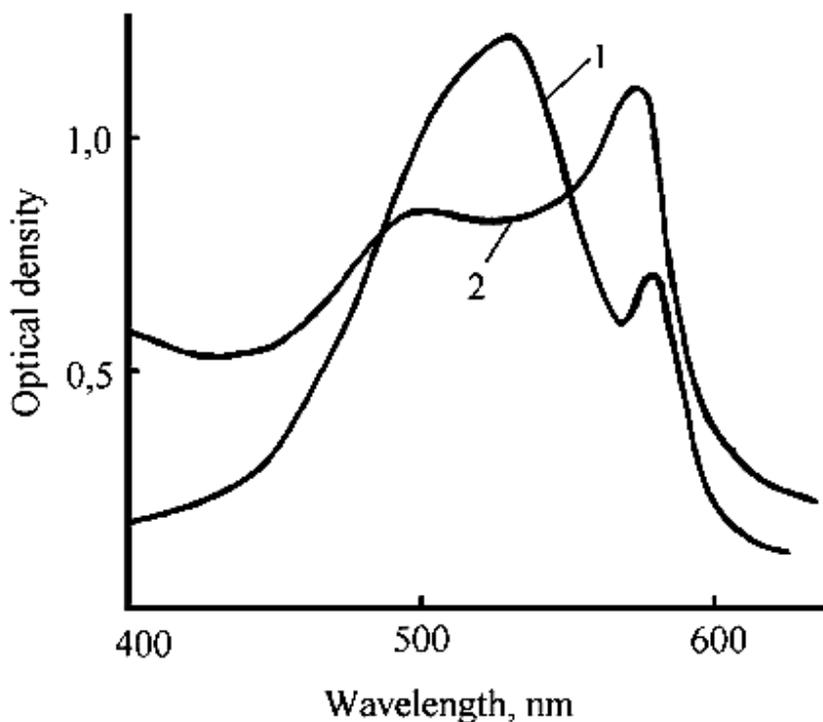


Fig. 3: Absorption spectra of dyes F490 (1) and F439 (2) in oriented CLC. Layer thickness 50 μm , concentration 0.1%.

In this class of dyes, we studied four dyes (No 4-7 in Table 2) with maximal absorption at 560-570 nm and quantum yields of fluorescence in ethanol solution 40-70 %. During dissolving in CLC at heating to the temperatures 10-20°C above T_{ph} , the dyes F 444 and F 439 were found slightly soluble in the used mixture of CLC, and, as it is shown in Fig.3 (curve 2), at 0.1% concentrations, in their optical absorption spectra intensive short-wave absorption arises, and this is accompanied with considerable decrease of the quantum yield (Table 2). In the cells with 50 μm thickness, optical densities of dyes at $\lambda=530$ nm were not greater than 0.8-1.0 for 0.1% concentration. The increase of the concentration of the dye practically did not lead to any increase of the absorption at $\lambda=530$ nm, instead of this, the absorption in the short-wave shoulder in the 400 nm region increased, which is the indication of the increasing amount of the aggregates of the dye molecules. The lasing in the planar texture of CLC in such conditions was not obtained in all the used range of intensities of excitation. The dyes F 427 and F 490 (Fig. 3, curve 1) had essentially better solubility in CLC, and lasing was obtained for this dyes at optical densities 0.8-1.0 in the planar texture of CLC with low threshold intensities of excitation (Table 2).

When comparing the absorption spectra of phenolone dyes presented in Fig.3, one can note that the increase of absorption in the 400 nm region for of dye F 439, as well as its low solubility indicate the aggregation of its molecules. This is confirmed also by disordering of the planar texture of CLC which is manifested in the broadening of the SR band with maximum in the 580 nm region and their decrease in transmission on its long-wave edge ($\lambda > 620$ nm). In the optical absorption spectra of dyes F 490 and F 427, for which lasing with low threshold was obtained, which have absorption maxima close to that for F 439, the short-wave shoulder in the 400 nm region is absent, and the absorption on the edge of the SR band is essentially smaller (Fig. 3, curve 1).

When analysing the data presented in Tables 1 and 2, we should note that, at concentration of dyes in CLC equal to 0.1%, the quantum yield for the most part of the dyes decreases as compared with the ethanol solutions. With exception of ketocyanines, the quantum yield and phototropic transformations of which in CLC are typical for non polar solvents, one can regard the aggregation of the molecules of the dyes as the main cause of the decrease of the intensity of their fluorescence in CLC. It is manifested in the appearance of new short-wave bands in the absorption spectra of rhodamine 6G and dyes F 439 and F 444, as well as in slump of their quantum yield (Tables 1 and 2). For the dyes in which signs of association in CLC are absent (No 6-7), one observes the increase of quantum yield of fluorescence. It is caused by great viscosity of such a matrix which leads to the decrease of the rate of the radiation less deactivation of the excited state of the molecules and hinders the processes of their conformational transformation.

These differences in the spectral and lasing characteristics of the electro neutral dyes of phenolone type can be explained with the difference in their spatial structures. Two groups of phenolone dyes differ in the structure of substituent group at the nitrogen atom in the phenolone core. For non lasing dyes (No 4 and 5, Table 2), such substituent is the methyl group (CH_3), and for lasing dyes (No 6 and 7), this is cyclohexyl group (C_6H_{11}). The obtained data indicate that precisely in the presence of the cyclohexyl group at the nitrogen atom of the molecule of the dye no clear aggregation of such molecules in their concentrated solutions in CLC is observed. As it is known [12,17], the presence of bulky end substituent group (the cyclohexyl group is non planar and belongs to such substituent) hinders coming the dye molecules together to such distances between them for which the formation of the sandwich like aggregate structure is possible. In contrast with the cyclohexyl group, the methyl group at the nitrogen atom of the phenolone core, due to its small volume, allows coming the dye molecules together and forming of their aggregates at high concentrations. In addition to steroidal hindrances for aggregation of the molecules, the cyclohexyl groups also increase the solubility of the dyes [17], and such increase is observed for the dyes F 490 and F 427.

CONCLUSION

The study of the spectral properties of lasing dyes in CLC also have shown that ionic dyes are scarcely suitable for the activation of the steroid type CLC. At 0.1-0.3% concentrations which are necessary for functioning of DFB laser, the molecules of ionic dye exist in such solution mainly as aggregates, which leads to the abrupt decrease of the quantum yield and does not ensure the achievement of the lasing threshold. For neutral phenolone dyes, the presence of bulky groups at the nitrogen atom of the phenolone core makes it possible to reduce to minimum the association of their molecules in concentrated solutions in CLC and to obtain lasing of DFB laser with low threshold intensities of excitation. It is determined for the first time that, notwithstanding the two order increase of concentration of such dye in the liquid crystal, its quantum yield essentially increases in comparison with diluted isotropic solution. Exactly this type of dyes is the most prospective for activation of CLC and improving the lasing characteristics of the DFB laser on its basis.

ACKNOWLEDGMENTS

We are very grateful to E.A.Lukyanets for leaving of phenolone dyes, Yu.A. Slominsky for leaving of ketocyanine dyes and A.A. Ischenko for valuable discussion.

This study was supported by Competitive Programm of Presidium of NAS of Ukraine (Project # VZ-94) and Ukrainian Foundation for Basic Research (project # 02. 07/145).

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