
MOLECULAR
SPECTROSCOPY

Photoluminescence of Pentyl-Cyanobiphenyl in Liquid-Crystal and Solid-Crystal States

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Abstract—The stationary and time-resolved photoluminescence spectra of *n*-pentyl-*n*'-cyanobiphenyl (5CB) are studied in a mesophase and solid-crystal state. The photoluminescence spectra of 5CB are determined by the molecular configuration and the intramolecular charge transfer in the excited state. It is shown that in the mesophase and solid-crystal state, 5CB exhibits along with monomer radiation at least two types of excimer radiation from different pre-dimer states. © 2000 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Photoluminescence of *n*-pentyl-*n*'-cyanobiphenyl (5CB) in liquid-crystal and solid-crystal states has been studied in papers [1–6]. It has been assumed that the fluorescence of 5CB is determined both by monomer and excimer emission. The authors [1–6] considered excimer emission of one type at 410 nm, which is typical for 5CB solutions. In [6], the dependence of the ratio of the monomer and excimer components on the emitting layer thickness was observed. At the same time, the data on the relation of the monomer and excimer emission spectra of 5CB with photoconformation transitions in this molecule and the intramolecular charge transfer in it are scarce.

In this paper, we measured the luminescence excitation spectra and time-resolved luminescence spectra and explained our results within the framework of the model of conformation rearrangement of 5CB molecules upon optical excitation. We studied the influence of the intramolecular charge transfer on the time-resolved spectra and luminescence kinetics of 5CB in a mesophase and a solid crystal state. We found that both in liquid-crystal and solid-crystal phases, there exist, along with the monomer emission, at least two types of excimer emission, which differ by their spectra and lifetimes.

EXPERIMENTAL

We studied *n*-pentyl-*n*'-cyanobiphenyl (Merk, Germany). This compound has a nematic phase in the temperature range from 18 to 35°C. Below 18°C, 5CB crystallizes, and above 35°C, it transforms to the isotropic state [2].

The luminescence excitation spectra were measured with a Hitachi MPF-4 spectrophotometer. The stationary and time-resolved luminescence spectra were recorded with an SPM-2 monochromator with a photoelectric attachment. The spectral slit width was 0.2–

0.4 nm. The luminescence was excited by a 337.1-nm pulsed nitrogen laser with a pulse repetition rate of 100 Hz, a pulse duration of 10 ns, and a pulse power of 5 kW.

The time-resolved luminescence spectra were recorded using a 0.1-ns gating system. The luminescence kinetics and luminescence spectra were recorded with different time delays t_d relative to the laser pulse maximum. To improve the time resolution, the luminescence spectra were detected at the initial moment after excitation at the leading edge of the laser pulse (negative values of t_d). Because of a high steepness of the leading edge of the laser pulse, the duration of excitation of a sample under study for $t_d = -4$ ns was equal to 0.7 ns. The decay curves were analyzed by recording the shape $G(t)$ of the laser pulse and the luminescence decay curves at different wavelengths. This ensured the determination of the lifetime τ of luminescence with an accuracy not worse than 0.1 ns. The experimental decay curves were processed using the method of curve catalog and parameter analysis [6, 7]. In this method, a convolution of the response function $G(t)$ with an arbitrary decay function $F(t)$ is calculated for different values of parameters and the calculated curve is selected that provides the best fit of the experimental luminescence decay curve. In our case, the experimental decay curve was approximated by a convolution of the exciting pulse with a sum of exponentials [$A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$] (where $\tau_2 > \tau_1$) or by one exponential $A_1 \exp(-t/\tau_1)$. The value of τ_1 was determined from the half-widths of the exciting pulse and the decay curve, and the value of τ_2 was determined from the tail of the decay curve. Upon detection of the luminescence kinetics of reference compounds with τ shorter than 0.1 ns, the laser and luminescence pulses coincided. For $\tau > 0.1$ ns, the luminescence pulse shifted relative to the laser pulse, which allowed us to measure the luminescence decay time above 0.1 ns.

RESULTS AND DISCUSSION

Luminescence Excitation Spectra

The luminescence excitation spectrum is the dependence of the luminescence intensity, which is detected at a certain wavelength, on the exciting light wavelength for a constant flux of photons incident on a sample. In the case of a weakly absorbing sample, the shape of the luminescence excitation spectrum coincides with that of the absorption spectrum. Indeed, the luminescence excitation spectrum is determined by a fraction of the light absorbed at different wavelengths, which, neglecting the correction for the light reflection, is

$$I_{\text{fl}}/I_0 = \varphi(1 - T). \quad (1)$$

Here, I_{fl} is the luminescence intensity, I_0 is the light intensity incident on a sample, φ is the quantum yield of luminescence, and T is the sample transmission. For $kd \ll 1$, where k is the absorption coefficient and d is the sample thickness, we have $I_{\text{fl}}/I_0 = \varphi kd$. It is assumed that the quantum yield φ for organic materials is independent of the exciting light wavelength. For an optical density lower than 0.1, the quantity $(1 - T)$ is proportional to the optical density with an accuracy of $\pm 5\%$.

We studied luminescence excitation spectra and stationary luminescence spectra of 5CB layers of two types: (i) A thin layer of about 100 nm deposited on a silica substrate, which was preliminarily processed by a homotropic orientation substance and (ii) a thick

layer of about a few microns deposited on a silica substrate.

It is assumed that in both cases the condition $kd \ll 1$ is fulfilled. Figure 1 shows the luminescence spectra of thin (curve 1) and thick (curves 2 and 3) layers measured at 301 K. The thin and thick layers were excited at 280 (curve 2) and 330 nm (curve 3), respectively. As the excitation wavelength was decreased, the luminescence spectrum slightly shifted to the red and the intensity of the short-wavelength 375-nm band decreased. The luminescence spectra of thin and thick layers are different. The first spectrum exhibits bands with maxima at 340 and 375 nm, while the second one exhibits bands located at 375 and 395 nm.

Figure 2 shows the luminescence excitation spectra of 5CB layers. One can see that the shape of the spectrum of the thin layer (curves 1 and 2) depends on the detection wavelength, the intensity of the short-wavelength wing being increased with increasing detection wavelength. For $\lambda_{\text{fl}} = 340$ nm, the luminescence excitation spectrum of the thin layer is similar to the absorption and luminescence excitation spectra of 5CB solutions and represents a structureless band with a maximum at 278 nm. According to [3, 5], the luminescence spectrum of the 5CB solution represents a structureless band with a maximum at 330–340 nm, depending on the solvent. This suggests that the 340-nm band observed in luminescence spectra of thin 5CB layers is related to emission of individual molecules. When the

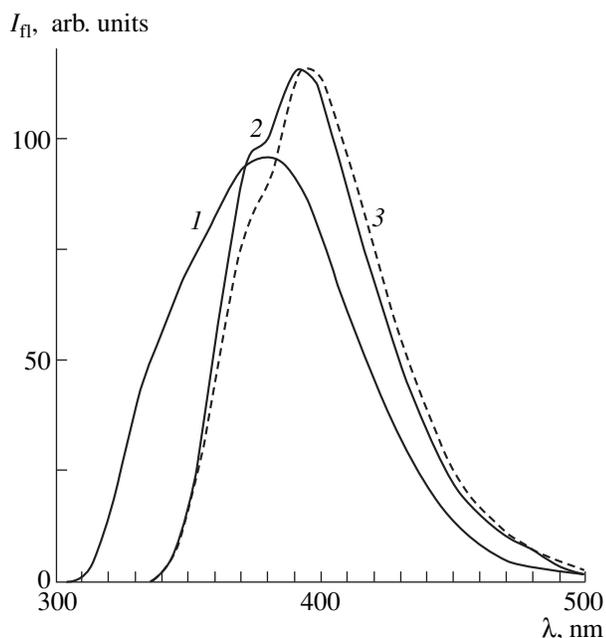


Fig. 1. Stationary photoluminescence spectra of (1) thin and (2, 3) thick layers of 5CB excited at (1, 2) 280 and (3) 330 nm at 301 K.

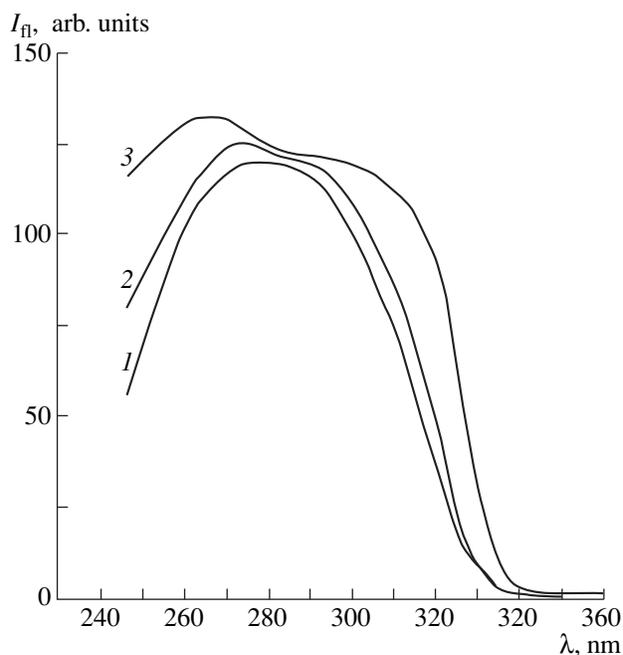


Fig. 2. Photoluminescence excitation spectra of (1, 2) thin and (3) thick layers of 5CB in the liquid-crystal state detected at (1) 340, (2) 370, and (3) 380 and 400 nm at 301 K.

luminescence excitation spectrum was detected at 370 nm (curve 2), a new band appeared at 265 nm.

The luminescence excitation spectrum of the thick 5CB layer detected at 380 nm (curve 3) exhibits two bands with maxima at 265 and 300 nm. This spectrum agrees well with the absorption spectrum of 5CB [1, 2, 4], which also has two bands with maxima at 265 and 300 nm. Upon detection of luminescence at the wavelength 400 nm, the intensity of the 265-nm band slightly increases compared to that observed upon detection at 380 nm and a weak shoulder is observed in the long-wavelength region (335–380 nm) whose intensity increases with increasing thickness of the liquid crystal. Upon excitation of the layer by a mercury lamp at 365 nm, intense luminescence was observed with a maximum at 405 nm.

Before proceeding to the discussion of the spectra presented in Figs. 1 and 2, we consider a number of factors that may affect the electronic properties of the 5CB molecule. These are the structure of the molecule in the ground and excited states, the intramolecular charge transfer in the excited state, and the mixing of neutral and polar molecular states upon optical excitation.

We assume that 5CB molecules have different geometry and, hence, different adiabatic potentials in different excited states. It follows from the data reported in the literature that the degree of conjugation of benzene rings changes upon the conformation transition of biphenyl molecules or their derivatives. The angle between the benzene ring planes in the biphenyl molecule in the ground and excited states in solutions at room temperature is 20°–40° and 0°–20°, respectively [8]. The cyano-biphenyl molecules in the ground state are also nonplanar, the planes of their benzene rings being turned by an angle of 30°–36° around the interring bond [9].

The electronic properties of the 5CB molecule in the ground and excited states depend on the asymmetry of conjugated fragments and intramolecular charge transfer in the excited state. In the case of a large twisting angle, the electronic subsystems of cyano-benzene and benzene fragments of 5CB can be treated as independent. The electron density in the molecule in the ground state is displaced to the cyano group, which is a good acceptor (A) of electrons. Benzene rings play the role of donors (D) in the 5CB molecule. The dipole moment of the 5CB molecule in the ground state is 3.9 D [10, 11] and increases substantially in the excited state [12].

The value of the dipole moment and the rate of charge transfer between a donor and an acceptor in the 5CB molecule in the excited state depend on its conformation and the polarity of the environment. We can assume that 5CB molecules in the excited singlet state can have (like biphenyl) different configurations with the twisting angle varying from 0° to 30°. The nonplanar configuration of the excited 5CB molecule in a polar medium can be stabilized due to the orientation polarization. The value of the dipole moment and the

lifetime of the excited molecule in the nonplanar conformation can substantially increase due to the localization of charges on the cyano group and the benzene ring conjugated with it. In the case of a planar conformation (due to a high conjugation of donors and acceptors in the molecule), the charge localization on them is hindered and charges recombine with a high rate. This results in the decrease in the lifetime and dipole moment in the excited state.

The excited state Ψ of molecules with the intramolecular charge transfer can be represented as a superposition of the locally excited state $\Phi_f(A\dots D^*)$, the charge transfer state $\Phi_I(A^-\dots D^+)$, and a set of molecular vibronic states χ_v [13–15]:

$$\Psi = C_1\Phi_f + C_2\Phi_I + \sum C_v\chi_v. \quad (2)$$

The similarity of the luminescence excitation spectra and absorption spectra and a large Stokes shift of the luminescence spectra suggest that, at the initial moment after the UV excitation into the absorption band, the 5CB molecule finds itself with a high probability in the locally excited Franck–Condon state Φ_f , whereas the luminescent state Φ_I appears only in the course of time. The latter term in (2) characterizes the competing channel of the intramolecular relaxation, whose specific weight is the quantum yield of the intramolecular ionization (D^+A^-). If the rate of the intramolecular charge transfer is much greater than the frequency of molecular vibrations, the electronic state of the molecule can be represented by the wave function of form (2). If the excited molecule is located in a strongly polar medium and the intramolecular charge transfer is not accompanied by the vibrational relaxation but only by the orientation polarization, the polar Φ_I state can be realized. This occurs in polar solvents [16–18]. It is likely that this also takes place for 5CB in the liquid crystal phase owing to the large dielectric constant $\epsilon = 18.5$ [3].

We can find from luminescence excitation spectra presented in Fig. 2 the initial Franck–Condon Φ_f states involved in excitation of luminescence of the 5CB molecule. In the 5CB molecule in a polar solvent, the $A_1-{}^1L_a$ optical transitions polarized along the long molecular axis dominate [12]. The presence of two bands in the luminescence excitation spectrum reflects the fact that the 5CB molecule in the ground state is nonplanar. The longer-wavelength bands ($\lambda > 270$ nm) in luminescence excitation spectra can be related to excitation of luminescence of 5CB molecules via the cyano benzene fragment, while the short-wavelength bands ($\lambda < 270$ nm) can be related to excitation via the benzene ring.

We noted above that, upon optical excitation, the 5CB molecule tends to pass to a plane conformation. For this reason, the luminescence spectrum of a thin 5CB layer (curve 1 in Fig. 1) also exhibits, along with the 340-nm band related to twisted molecules, the 375-nm band related to emission of plane molecules.

We can assume that the 340-nm band corresponds to emission from the relaxed polar Φ_I state of the cyano benzene fragment. The 278-nm band in the luminescence excitation spectrum (curve 1 in Fig. 2) corresponds to the 340-nm band in the luminescence spectrum. The increase in the intensity of the short-wavelength wing of the 265-nm band upon detection of the luminescence excitation spectra at 375 nm (curve 2 in Fig. 2) can be explained by the fact that the probability of transformation of 5CB molecules to a plane conformation increases with increasing energy of the exciting photon.

We suppose that the difference between the luminescence and luminescence excitation spectra of thick and thin layers of 5CB (Figs. 1 and 2) can be caused to some degree by the reabsorption and bulk properties of the thick liquid crystal layer. The reabsorption of luminescence in the thick layer should result in a decrease in the intensity of the short-wavelength part of the spectrum, which can explain the disappearance of the 340-nm band. On the other hand, in a liquid crystal, which represents a strongly polar solution, upon excitation of 5CB molecules at 265 nm (curve 3 in Fig. 2), a strongly polar D^+A^- state can be stabilized due to effects of orientation polarization. In this state, the 5CB molecule does not transfer to a planar conformation, but remains twisted, and charges are localized on the cyano group and a remote benzene ring. This should result in a great Stokes shift of the luminescence spectrum. Indeed, upon excitation of luminescence by high-energy photons at 280 nm, the intensity of the short-wavelength 375-nm band in the luminescence spectrum decreases (curve 2 in Fig. 1), whereas the intensity of the long-wavelength 395-nm band increases. The relative enhancement of the 375-nm band (curve 2 in Fig. 1) with increasing excitation wavelength can be explained by the fact that the photon energy is insufficient for excitation of strongly twisted molecules, whereas molecules with the nearly planar conformation are efficiently excited.

Time-Resolved Luminescence Spectra of 5CB

Figure 3 shows the stationary (curve 1) and time-resolved (curves 2 and 3) luminescence spectra of 5CB measured in the liquid crystal phase at 301 K. The thickness of the liquid-crystal layer in an optical silica cell was 100 μm . For short time delays ($t_d = -4$ ns, curve 2), the luminescence spectrum exhibits two bands at 372 and 395 nm. The luminescence spectrum measured at $t_d = -4$ ns is related to the electronic excitations that underwent transitions to the lowest relaxed fluorescence states for 0–0.7 ns after excitation and that differ in their lifetimes. Upon variation of t_d from –4 to 0 ns, the shape of the spectrum almost did not change. The lifetime of luminescence in the region from 360 to 380 nm was 5.9 ns (Fig. 4, curve 4). The measurement of the luminescence kinetics at the maximum of the

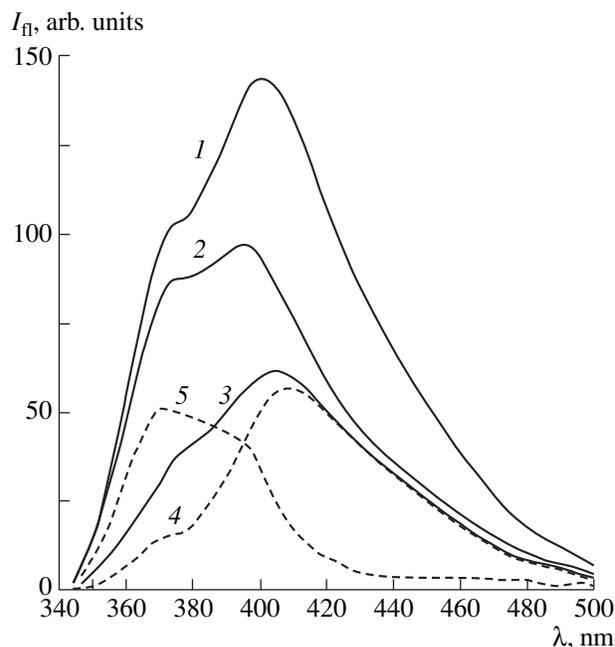


Fig. 3. (1) Stationary and (2, 3) time-resolved photoluminescence spectra of a 5CB liquid crystal at 301 K. (2) $t_d = -4$ ns; (3) $t_d = 15$ ns; (4) difference between spectra (1) and (2); and (5) difference between spectra (2) and (3).

405-nm band (curve 5 in Fig. 4) showed that it is determined by the emission components with $\tau_1 = 8.8$ ns and $\tau_2 = 22$ ns. Because of the difference in the lifetimes of the excited states, the intensity of the short-wavelength wing decreases with increasing t_d to 15 ns (Fig. 3, curve 3) and the spectrum exhibits two bands at 380 and 405 nm.

The stationary spectrum (Fig. 3, curve 1) exhibits two bands at 372 and 400 nm. Unlike the instant spectra, the stationary luminescence spectrum is determined by a superposition of all the emission components with different lifetimes. The stationary luminescence spectrum of 5CB in the liquid crystal phase (curve 1 in Fig. 3) has a component in the region $\lambda_{fl} > 380$ nm with $\tau_2 = 22$ ns. The emission spectrum of this component (curve 4 in Fig. 3) can be obtained by subtracting curve 2 from curve 1. One can see that the most intense band in this spectrum is located at 405 nm. This band can be assigned, as in [2–4], to the excimer emission of the first type. The lifetime of this excimer state is 22 ns. The integrated luminescence spectrum in the solid state virtually coincides with the instant spectrum measured for short t_d . The 405-nm emission band of 5CB in the solid state at 290 K has two components with $\tau_1 = 4.7$ ns and $\tau_2 = 7.5$ ns. The component with $\tau = 22$ ns, which we assigned to the excimer emission of the first type, substantially weakens upon transition from the liquid crystal to the solid state and disappears with increasing temperature. The decrease in the intensity of the excimer emission with decreasing temperature is

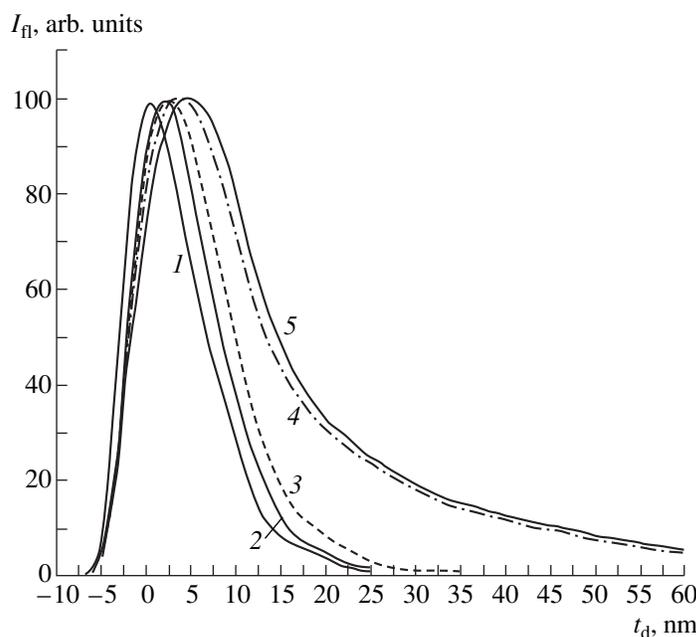


Fig. 4. Kinetics of (1) laser radiation and photoluminescence of 5CB in (2, 3) solid crystal and (4, 5) liquid crystal states detected at (1) 337.1, (2) 355–380 nm, (3) 405 nm at 4.2 K and (4) 380 and (5) 405 nm at 301 K.

caused by its activation nature, namely, by the presence of a potential barrier between an unexcited pair of molecules and the excimer [19]. The activation energy of the excimer emission of the first type is 6500 cm^{-1} [4]. The luminescence of liquid-crystal and solid-crystal

layers in the region from 350 to 380 nm can be assigned to the monomer emission. Because the lifetime of monomer emission is substantially shorter than that of the excimer emission, the spectrum of monomer luminescence can be obtained by subtracting curve 3 from curve 2 (curve 5 in Fig. 3). As in the case of molecular emission, the 372-nm luminescence band of 5CB in the liquid-crystal phase represents emission of planar molecules.

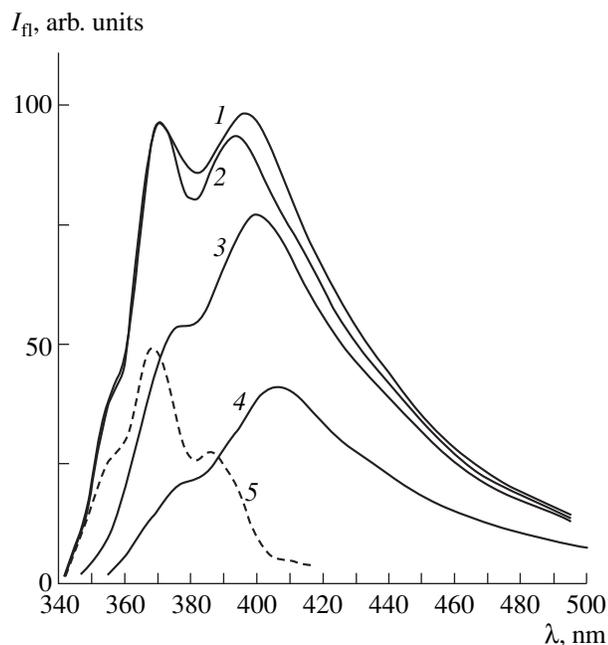


Fig. 5. (1) Stationary and (2–4) time resolved photoluminescence spectra of a 5CB solid crystal at 4.2 K. (2) $t_d = -4$, (3) 10, and (4) 20 ns. (5) Difference between spectra (2) and (3).

The stationary luminescence spectrum (curve 1 in Fig. 5) and the luminescence spectrum of 5CB in the solid state measured with a short time delay at 4.2 K almost coincide. The similarity of the stationary and instant ($t_d = -4 \text{ ns}$) luminescence spectra reflects the fact that all the excited electronic states in the solid crystal relax to the lowest luminescent states for 0–0.7 ns after the excitation. These states have different energies and lifetimes. For short delays ($t_d = -4 \text{ ns}$, curve 2), the 355- and 370-nm bands are observed in the short-wavelength region, which can be related to monomer emission. The lifetime of luminescence in the region from 355 to 380 nm is 1.5 ns. The luminescence kinetics at 400 nm is characterized by the lifetimes $\tau_1 = 1.5 \text{ ns}$ and $\tau_2 = 3.4 \text{ ns}$ (Fig. 4, curve 3). Because of the difference between the lifetimes of luminescence in the short- and long-wavelength spectral regions, the luminescence intensity in the short-wavelength region decreases with increasing t_d to 10 ns (curve 3) and the 380-nm and 400-nm bands remain in the spectrum. As t_d is further increased (curve 4), the long-wavelength band shifts to 405 nm. The emission of a 5CB solid crystal at $\lambda_{fl} > 390 \text{ nm}$ can be assigned to the excimer

emission of the second type with the lifetime $\tau_2 = 3.4$ ns. Excimer emission of the second type can be also observed upon excitation of liquid-crystal and solid-crystal 5CB samples not only in the region of strong absorption but beyond the absorption edge (at $\lambda > 380$ nm). As was noted above, the luminescence excitation spectra of thin layers of 5CB exhibit a structureless shoulder in the region from 340 to 380 nm, which is related to weak absorption of light. The possibility of simultaneously observing absorption and emission in this spectral region can be associated with pre-dimer states, a fraction of which form physical dimers already in the ground state. This results in the spectral overlap of monomer and dimer emissions, which can only be distinguished by their lifetimes. The lifetime of the 380-nm emission band is 1.5 ns; i.e., it coincides with that of the 370-nm band. The spectrum of the fast emission component of a 5CB solid crystal (curve 5) can be obtained, as for the liquid crystal, by subtracting curve 3 from curve 2. This spectrum exhibits emission bands with maxima at 355, 368, and 385 nm. This spectrum is similar to the spectrum of 5CB in ethanol at 77 K.

The presence of two types of isomers of 5CB can be explained by the presence of two types of pre-dimer states, which differ in the intermolecular distance and the mutual arrangement of molecules in the ground state. In turn, two types of packing of molecules in pre-dimer pairs can be determined by the planar or twisted conformations of molecules forming a pair. The excimer emission at 405 nm with $\tau_2 = 22$ ns, which is observed in the liquid-crystal phase, can be related to the pre-dimer states of the first type. In these states, the ground-state molecules in a pair are widely separated. For this reason, the interaction between these molecules in the ground state is weak. Upon excitation, these molecules can come within the equilibrium van der Waals distance of each other and form the excimer state. Unlike in a liquid crystal, such an approach of the molecules in pre-dimers pairs in solid crystals is hindered and only monomer luminescence is observed at low temperatures in the latter case. These are the 355- and 372-nm bands observed for small values of t_d (curve 2 in Fig. 5).

The pre-dimer states of the second type are typical for a 5CB solid crystal. Because of the planar conformation, the orientation of molecules in a pair, as for pyrene crystals [19], is close to the sandwich one already in the ground state. Unlike the pre-dimer pairs of the first type, the lowering of temperature does not prevent the excimer formation. For this reason, the excimer emission can be observed from these pre-dimer states both in the mesophase and in solid crystals at low temperatures. The luminescence bands observed at 400–405 nm at 4.2 K (curves 2 and 3 in Fig. 5) can be related to the excimer emission of the second type. The dependence of the position of the excimer band on t_d can indicate the presence of the distribution of the pre-dimer configurations that differ in intermolecular

distance and the degree of the intermolecular overlap. The 380-nm luminescence band, which is observed along with the 400-nm band at 4.2 K, can be related to the monomer emission of planar 5CB molecules, which are present in the ground state in a crystal. However, weak absorption and emission at 380 nm cannot be definitely assigned to monomers. The absorption and emission at 380 nm can also be related to physical dimers, which can exist in the ground state.

CONCLUSIONS

We studied the luminescence spectra of 5CB in liquid-crystal and solid-crystal states. We found that the luminescence spectra depend on the intramolecular charge transfer and molecular geometry in the ground and excited states. The luminescence bands of monomers are located in the spectral region below 400 nm. The structure of the monomer luminescence spectrum is determined by the presence of several excited states, which differ in the degree of intramolecular charge transfer in the excited state. The excimer emission is observed in the long-wavelength region above 400 nm. We found that there exist at least two types of pre-dimer states from which excimer emission is observed. The excimer emission of the first type is observed at 408 nm in the liquid-crystal phase and is characterized by the long lifetime $\tau = 22$ ns. The excimer emission of the second type is observed both in liquid-crystal and solid-crystal phases. A maximum of this emission in the solid-crystal phase is located at 400–405 nm, and the lifetime is 3.4 ns at 4.2 K. Unlike pre-dimer states of the first type, in which the distance between molecules is quite large, the pre-dimer states of the second type can have the sandwich or close structure already in the ground state.

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