

Effects of UV radiation on selective reflection and dielectric properties of cholesterol ester mixtures with photoactive nematics

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Cholesteric liquid crystal mixtures containing nematic ZhK-440 (comprising alkyl- and alkoxy azoxybenzenes) and cholesterol esters were studied as examples of UV-sensitive systems based on a photoactive nematic hosts and non-photoactive chiral components (ChC). The ChC concentration was varied within 35–90 %, resulting in selective reflection with maximum λ_{max} in the visible range and different character of its variation with temperature. At high ChC concentrations, UV-induced λ_{max} (helical pitch) variation corresponded to the sign of $d\lambda_{max}/dT$ in the initial mixture, with formation of non-mesogenic and non-chiral *cis*-isomer leading to depression of the isotropic transition temperature. At lower ChC concentrations, λ_{max} decreased in all cases, regardless of the $d\lambda_{max}/dT$ sign. A theoretical explanation of this peculiar case of helical twisting is offered, implying a possibility of the effective chirality of ordered *cis*-molecules. The assumptions made are in agreement with UV-induced changes in dielectric permittivity. Prospects of practical applications of the systems studied are discussed.

Жидкокристаллические смеси эфиров холестерина и нематиков на основе азоксибензолов рассмотрены как примеры УФ-чувствительных систем с фотоактивной нематической матрицей и неактивных хиральных компонентов (ХК). Содержание ХК варьировали в пределах 35–90 %, что обеспечивало селективное отражение с максимумом λ_{max} в видимой области и различный характер его изменения с температурой. При высоких концентрациях ХК УФ-индуцированное изменение λ_{max} (шага спирали) соответствовало знаку $d\lambda_{max}/dT$ исходной смеси, со снижением температуры изотропного перехода вследствие образования немезогенных и нехиральных *цис*-изомеров. При более низких концентрациях ХК λ_{max} снижалась во всех случаях независимо от знака $d\lambda_{max}/dT$. Предложено объяснение такой особенности поведения спирального закручивания на основе представлений об эффективной хиральности упорядоченных *цис*-молекул. Сделанные предположения согласуются с УФ-индуцированными изменениями диэлектрической проницаемости. Обсуждаются возможности практического применения исследованных систем.

1. Introduction

It has been long known that in cholesteric mixtures containing azo- or azoxybenzene, as well as their derivatives, the wavelength of maximum selective re-

flection λ_{max} can be varied as an effect of UV-irradiation. Such behaviour, which was first reported in [1] and revisited in more recent papers [2], is attributed to the photoinduced *trans-cis* isomerization of the photoactive compound. The transformation

is reversible, and the initial λ_{max} value can be largely restored under irradiation at higher wavelengths, after heating to the isotropic phase, or just after storage. Recently, substantial interest has been noted in this phenomenon due to application prospects of such mixtures in tunable cholesteric dye lasers controlled by UV radiation [3, 4]. Reversible changes in λ_{max} were studied in detail for mixtures containing nematic azoxy compounds and chiral components (which could be either cholesterol esters or chiral dopants normally used for induction of helical twisting) [5, 6]. *Trans-cis* isomerization of azoxybenzene liquid crystals was studied in [7], with formation of *cis*-isomers (with much smaller molecular anisotropy) leading to substantial lowering of the orientation order and depression of isotropic transition temperatures. Similar results for azobenzene-based nematics with chiral components were reported in [8, 9] for different irradiation conditions.

A remarkable feature of the observed UV-induced changes in λ_{max} is that it is shifted to shorter wavelengths under primary irradiation. This means that the helical pitch p ($\lambda_{max} = np$, where n is the average refraction index) is decreased, i.e., additional helical twisting appears. This contradicts what could be expected from general notions of cholesteric mesophases – it is not clear why formation of non-chiral and non-mesogenic *cis*-molecules should increase the helical twisting and not lead to unwinding of the helix. A possible explanation can be given in the case when λ_{max} of the initial mixture decreases with temperature ($\partial\lambda_{max}/\partial T < 0$) – lower orientational order caused either by the formed *cis*-molecules or by an increase in temperature affects the helical twisting in a similar way. In most of the above-noted papers, no data on $\lambda_{max}(T)$ are given. In a seemingly sole study where this aspect was considered [6], the observed shifts of λ_{max} under UV radiation were always negative, regardless of the sign of $\partial\lambda_{max}/\partial T$. It should also be noted that the negative sign of UV-induced λ_{max} shifts was characteristic for chiral components of both steroid (cholesterol esters) and non-steroid nature, which excluded possible explanations based on the extra twisting known for nematic-cholesteric mixtures [11, 12]. To clear up the situation, additional experimental data were obviously needed. In this study, we measured UV-induced λ_{max}

shifts for mixtures of cholesterol esters containing different concentration of azoxy nematics and showing different $\lambda_{max}(T)$ behavior.

2. Materials and methods

The photosensitive nematic component used was a 2:1 mixture of 4-*n*-butyl-4'-methoxyazoxybenzene and 4-*n*-butyl-4'-heptanoylazoxybenzene (liquid crystal ZhK-440, NIOPIK, Russia, nematic range from -5°C to 75°C). As chiral component, we used a cholesteric mixture M23 containing 82 % cholesteryl oleyl carbonate (Aldrich, USA) and 18 % cholesteryl chloride (Chemical Reagents Plant, Kharkiv, Ukraine).

The λ_{max} values of selective reflection peaks were determined from optical transmission spectra measured in a 10 μm thick temperature-controlled cell using a Hitachi 330 spectrophotometer in a similar way as described previously [13]. The appropriate quantities of component substances were mixed in the state of isotropic liquid, and the mixture obtained was introduced between the measurement cell walls by capillary forces. The cell thickness was set by Mylar spacers. To ensure good planar texture with clear and reproducible selective reflection peaks, before introduction of the mixture the cell walls were immersed in a 0.5 % water solution of polyvinyl alcohol, dried and rubbed in one direction by a soft tissue, ensuring good planar texture with clear and reproducible selective reflection peaks.

UV irradiation was carried out using a UV illuminator based on a DRT-240 mercury lamp. The energy illuminance dose values were set by varying the exposure time and the distance between the cell and the illuminator output window [14]. Two types of filters were used: UVC-2 (transparent in the 250–370 nm range) and ZhS-10 (transparent above 400 nm).

3. Results and discussion

Typical examples of $\lambda_{max}(T)$ dependences measured for different concentrations of nematic ZhK-440 and cholesteric M23 before and after UV irradiation are shown in Fig. 1. Characteristic features of the results obtained can be summarized as follows. At relatively high concentrations of ZhK-440 (65 %) shifted to shorter wavelengths under UV irradiation, in the same way as it was noted in [5–10]. The shift, as it could be expected, increased with the exposure dose. The use of a UVC-2 filter practically

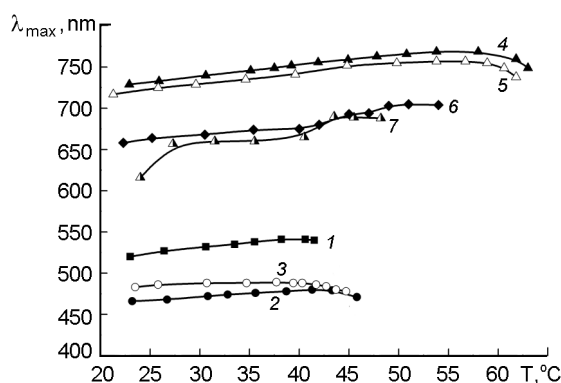


Fig. 1. Selective reflection maximum λ_{max} as function of temperature for cholesteric systems: 1 — M23 (mixture of cholesterol derivatives), 2,3 — 90 % M23 + 10 % nematic ZhK440, 4-7 — 65 % ZhK-440 + 35 % M23 before (2,4) and after (3,5,6,7) UV irradiation. Irradiation conditions: 3,5 — 2 mW/cm², filter UVC-2; 6 — 10 mW/cm², without filter; 7 — 10 mW/cm², filter UVC-2.

did not affect the observed behaviour. On the contrary, at low concentrations of ZhK-440 (~10 %) λ_{max} shifted to longer wavelengths in conformity with the sign of $\partial\lambda_{max}/\partial T$. It could be assumed that the total observed shift of λ_{max} was a sum of at least two contributions of different nature. At small concentrations of ZhK-440 (i.e., at small concentrations of *cis*-molecules formed) the system behaves itself as a "normal" cholesteric, while at larger concentrations *cis*-molecules appear to induce an anomalous contribution to helical twisting. Analyzing the data of [6, 10], a certain correlation can be noted between the UV-induced λ_{max} shift and the value of $\partial\lambda_{max}/\partial T$ (though no cases of UV-induced shifts towards longer wavelengths were reported). Moreover, it appears (from the same data) that "blue" λ_{max} shifts are less pronounced for systems containing cholesterol esters. This is quite natural, since *cis*-molecules, with their smaller anisometry, do not give rise to extra twisting characteristic for nematic-cholesteric mixtures [11, 12]; thus, in the presence of cholesterol esters, UV irradiation should decrease the twisting originating from this factor. Still, the "blue" shift persisted, and it should be due to a cause that has never been considered in the existing theories of helical twisting.

To make sure that conditions of our experiments were essentially similar to those of [5–10], our UV-irradiated samples where *cis*-isomers had been presumably formed

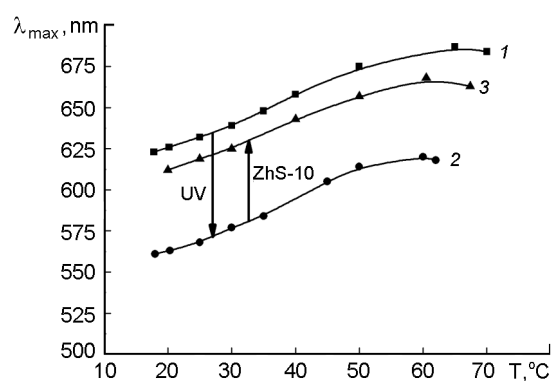


Fig. 2. Selective reflection maximum λ_{max} as function of temperature for 25 % M5 + 75 % ZhK-440 before (1) and after (2,3) irradiation. 2 — UV irradiation without filter, 10 mW/cm²; 3 — light irradiation using filter ZhS-10, 10 mW/cm².

were irradiated by light with longer wavelength; specifically, we used our illuminator with a ZhS-10 filter transmitting light only above ~400 nm (Fig. 2). As it could be expected, the initial state was largely restored (though the efficiency of this "inverse" process of *cis-trans* transformation was much lower).

To explain the anomalous "blue" shift of λ_{max} , the following path of reasoning is proposed. The *cis*-molecules formed, as distinct from their *trans* precursors, have no distinguished geometric anisometry, and their structure is essentially planar [7]. In the conditions of the cholesteric phase with its strong local biaxiality [11], this can favor specific ordering features of the *cis*-molecules in the helically twisted matrix. Namely, while *trans*-molecules are almost free to rotate around their long axis (as is typical for ordinary nematics), the corresponding rotation of *cis*-molecules is substantially hindered; in fact, they are expected to be predominantly stabilized in two different orientations, i.e., with "up" and "down" directions of their short molecular axes. If we consider each of these orientation as a separate molecular species, they should be considered as effectively chiral. (This idea is, in fact, not new — in relationship to other types of isomerizable nematic molecules, it was earlier proposed in [15, 16]).

There is a well-known principle of the "closest packing" forwarded by Kitaigorodski [17], according to which a molecule in the crystalline phase tends to assume the conformation that ensures the highest packing density. A similar principle was pro-

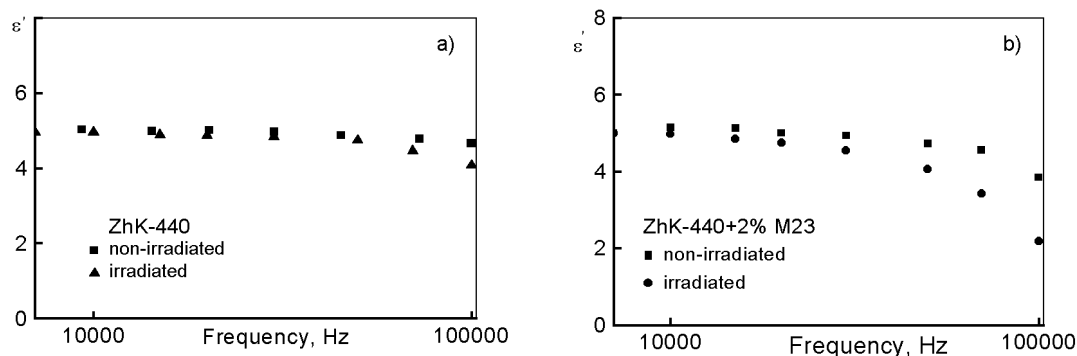


Fig. 3. Dielectric permittivity as function of frequency for ZhK-440 (a) and ZhK-440 + 2 % M23 (b) before and after UV irradiation.

posed for liquid crystalline orientational ordering – a molecule tends to assume the conformation ensuring the highest molecular anisotropy (this is realized, e.g., for long alkyl chains in the nematic matrix) [18]. We can suppose that in a similar way a molecule introduced into the cholesteric mesophase tends to assume the orientation that corresponds to the sense of the already formed cholesteric helix. Hence the *cis*-isomer molecules of an azobenzene or azoxybenzene compound act as effectively chiral components, increasing the helical twisting and leading to smaller helical pitch and λ_{max} values shifted to smaller wavelengths.

To check the validity of our assumption, we studied dielectric permittivity ϵ as function of frequency f in systems of our type (i.e., azoxy nematics + cholesterol esters) before and after UV irradiation. Characteristic inflections are normally observed on $\epsilon(f)$ plots at certain f values that correspond to reorientation frequencies of anisometric molecules [19]. It could be expected that the loss of rotation freedom by azoxy *cis*-molecules formed in the cholesteric phase will be reflected in a shift of the characteristic fall of ϵ towards lower frequencies.

The experimental set-up for dielectric permittivity measurements was essentially the same as described in [20]. In the ZhK-440 + M23 system, M23 concentrations ensured helical pitch values of 2–8 μm determined by the Cano wedge method. UV irradiation conditions were similar to those used for induction of changes in λ_{max} as described above. The $\epsilon(f)$ dependences obtained are shown in Fig. 3.

Peculiar features of the experimental installation used set a limited frequency range (up to $\sim 4 \cdot 10^5$ Hz), which did not allow to reach the inflection point. How-

ever, it can be seen that the frequency of the "onset" of the decrease in ϵ is clearly shifted to smaller f values after UV irradiation when the chiral component is present.

4. Conclusion

Our results, though preliminary and qualitative, support our above-proposed picture explaining anomalous twisting behavior of mixtures of azoxy nematics and cholesterol esters under UV irradiation.

Still another conclusion follows from our results. As first shown in our study, the UV-induced helical pitch changes in mixtures of azoxy nematics and chiral components can be positive or negative, with the sign and magnitude of these changes can be easily adjusted by varying the component concentration. In combination with reversible character of these UV-induced effects, this makes the systems studied very promising for application in tunable dye lasers.

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Вплив УФ-опромінювання на селективне відбивання та діелектричні властивості сумішей естерів холестерину з фотоактивними нематиками

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Рідкокристалічні суміші естерів холестерину та нематиків на основі азоксибензолів розглянуто як приклади УФ-чутливих систем з фотоактивною нематичною матрицею та нефотоактивних хіральних компонентів (ХК). Вміст ХК варіювали у межах 35–90 % з отриманням селективного відбивання з максимумом λ_{max} у видимій області та різним характером його зміни з температурою. При високих концентраціях ХК, УФ-індукована зміна λ_{max} (кроку спіралі) відповідала знаку $d\lambda_{max}/dT$ вихідної суміші, зі зниженням температури ізотропного переходу внаслідок утворення немезогенних і нехіральних *цис*-ізомерів. При нижчих концентраціях ХК λ_{max} зменшувалася в усіх випадках, незалежно від знаку $d\lambda_{max}/dT$. Запропоновано пояснення такої особливої поведінки спірального закручування на основі уявлень про ефективну хіральність впорядкованих *цис*-молекул. Зроблені припущення узгоджуються з УФ-індукованими змінами діелектричної проникності. Обговорюються можливості практичного застосування досліджених систем.