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Development of personal biodosimeter of UV radiation based on vitamin D photosynthesis in nematic liquid crystal matrix

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Abstract. A new approach to the problem of personal UV biodosimeter is described. Nematic liquid crystal (LC-805) is converted into induced cholesteric phase using photosensitive chiral dopant of steroid biomolecules (7-dehydrocholesterol (provitamin D3) or 7-DHC-benzoate). Significant changes in optical characteristics of the LC films depending on the duration of UV exposure are observed as a result of UV initiated photoisomerizations that change helical twisting power of dopant molecules.

Keywords: UV dosimetry, photoresponsive materials, liquid crystals, provitamin D photoisomerization.

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1. Introduction

Molecular chirality offers intriguing possibility in the design of new photoactive organic materials. Conversion of nematic liquid crystals (LC) into chiral nematic (induced cholesteric) phase using a chiral dopant, and control of the structure and optical properties of LC phases by means of light play a central role in the development of molecular device and optical data storage systems. In a few cases reversible optical switching between nematic and cholesteric phase has been demonstrated [1-4].

This article discusses a possibility of applying such LC material doped with chiral biomolecule of provitamin D to dosimetry of biologically active UV radiation. It is known that solar (and artificial) UV radiation is liable for causing sunburn (erythema), premature skin aging and skin cancer. However, these acute and chronic effects only occur upon excessive UV exposures. In proper dose, UV sunlight plays an important positive biologic role initiating endogenous synthesis of vitamin D that is absolutely essential for the maintenance of healthy skeleton and bones [5]. Hence, personal control of biologically active UV dose is of critical importance for human health (especially in view of stratospheric ozone depletion).

The UVB portion of sunlight (280-315 nm) converts provitamin D into previtamin D which, in turn, undergoes a thermally induced isomerization into vitamin D. Well studied photoreaction of provitamin D in ethanol solution (model «*in vitro*») includes hexadiene ring-opening to form previtamin D and its further side photoconversions, the more important of which is *cis-trans* isomerization into tachysterol [6]. The idea of personal UV dosimeter lies in the insertion of chiral molecules of provitamin D into nematic liquid crystal and close inspection of its optical properties depending on the UV exposure. It is expected that the changes in helical twisting power of provitamin D molecules (as a result of UV irradiation) give rise to significant changes in optical characteristics of the cholesteric LC film.

2. Materials and methods

To comply with the requirements, the LC matrix should be transparent in UV range (250-350nm), thermally stable over the interval at least 10-40 °C, be a good solvent for 7-dehydrocholesterol (and related compounds) and be stable with respect to the visible light. Nematic LC-805 (1:1 mixture of 4-n-butyl-trans-cyclohexancarbon and 4-n-hexyl-trans-cyclohexancarbon) has been selected as a host matrix [7]. It was possible to induce the cholesteric phase by doping with 5 ÷ 10 wt.% of 7-DCH or 7-DHC-Benzoate (7-DHC-Bz) as evidenced by a papillary texture observed with polarized microscope.

The cholesteric mixture was filled into wedge-shaped cell (15×20 mm^2) with polyimide-coated glass walls of ~ 60 μm thickness. Close inspection of the behavior of the Grandjean-Cano stripes was carried out with polarized microscope to elucidate both the sample stability (under dark conditions and visible light irradiation) and the UV effects. The UV lamp EL-30 delivered integral intensity of 0.3 mW/cm^2 within

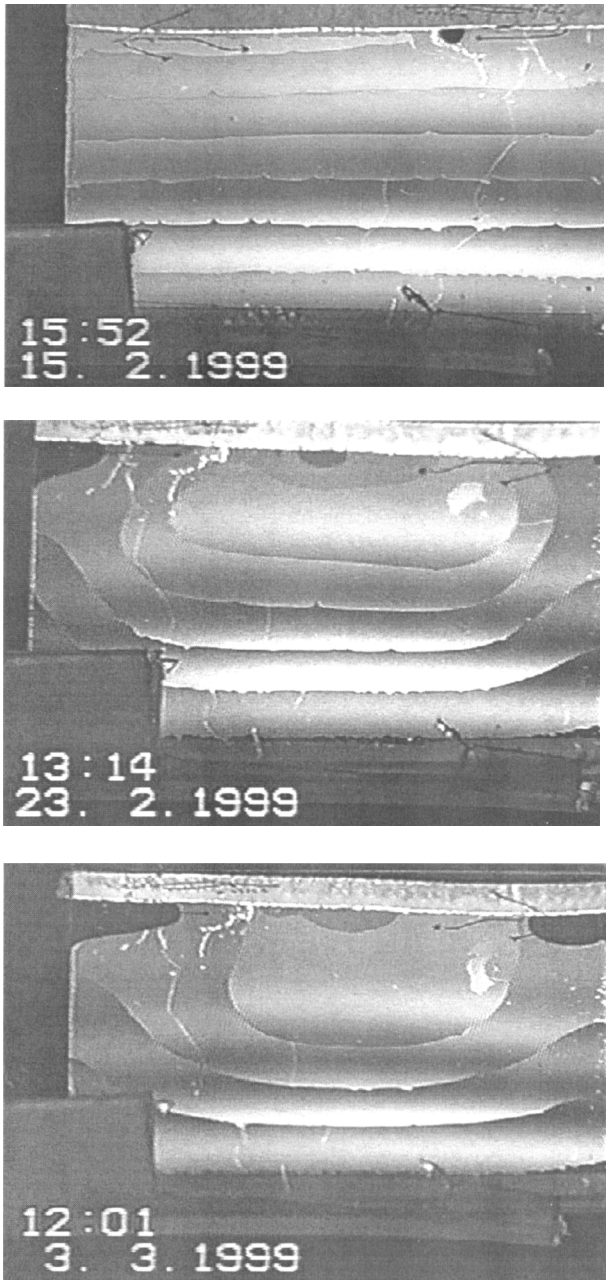

Fig.1. Decay of the cholesteric Cano structure in unsealed wedge-shaped cell depending on the storage time observed with polarizing microscope through crossed polarizers.

spectral range of 250-350 nm at the distance of 12 cm. In the course of UV irradiation only one half of the cell was illuminated, and the other half was protected with black paper. After fixed UV exposures the transmittance spectra of the both parts of the cell were recorded with KSVU-23 spectrometer in parallel with the microscope observations.

In addition, the microenvironment effect on the photoreaction course of 7-DHC and 7-DHC-Bz was investigated by comparison of the spectral kinetics in LC matrix with known spectral kinetics in ethanol solution.

3. Results and Discussion.

Well known dependence of the number of disclination Cano stripes in wedge-shaped cell on the concentration of chiral dopant was observed with polarized microscope. It was found that the number of the Cano stripes can reach $N_C = 14$ at best when the dopant concentration reaches 10 wt.% that corresponds to maximum solubility. The pitch of the cholesteric helix as well as helical twisting power (HTP) were determined for 7-DHC and 7-DHC-Bz using the Grandjean-Cano technique [8]. The helix is left-handed for both dopants and the HTP of 7-DHC and 7-DHC-Bz is equal in value ($-1.2\ \mu m^{-1} wt.\%^{-1}$).

In unsealed cell, on keeping in dark, the Cano stripes progressively declined in number with slow broadening starting from the cell borders (Fig. 1). We associate this instability with the loss of twisting power of chiral dopant by oxidation [9]. Figure 2 demonstrates that in case of 7-DHC degradation of the Cano stripes proceeds more slowly than in case of 7-DCH-Bz. To avoid oxidation, on the subsequent experiments the cell was carefully sticked along the perimeter, and the number of the Cano stripes was found to be unchanged in storage.

In view of the rather low HTP of the dopants the selective reflection band of the chiral LC phase is situated far enough from the visible range. Therefore effects of UV irradiation were studied by watching the Cano stripes behavior with simulteneous registration of the cell transmittance at $\lambda = 330$ nm to find a correlation with the dopant phototransformations.

Additionally the spectral kinetics was monitored within the spectral range 230-350 nm by sandwiched the LC mixture between two quartz plates. Comparison of the spectral kinetics of 7-DHC and 7-DHC-Bz in ethanol and in LC-805 matrix is shown in Fig. 3. One can readily see that in both cases incorporation of the molecule in LC matrix significantly intensifies *cis-trans* isomerization as evidenced by the increase of the absorbance at 280 nm and by the spectrum transformations intrinsic to tachysterol accumulation [10].

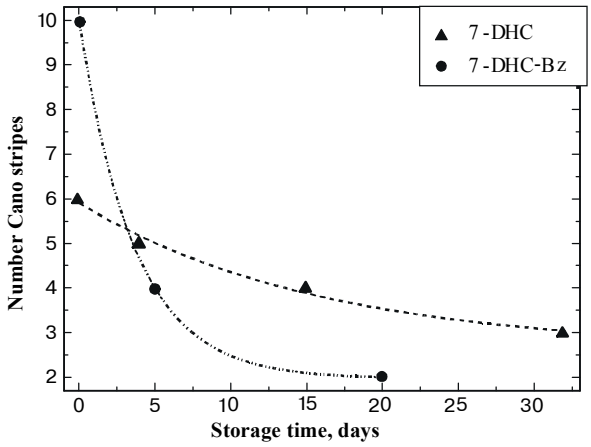

Fig.2. Dependence of the number of the Cano stripes on the storage time in unsealed cells (triangles – 7-DHC in LC-805, circles – 7-DHC-Bz in LC-805).

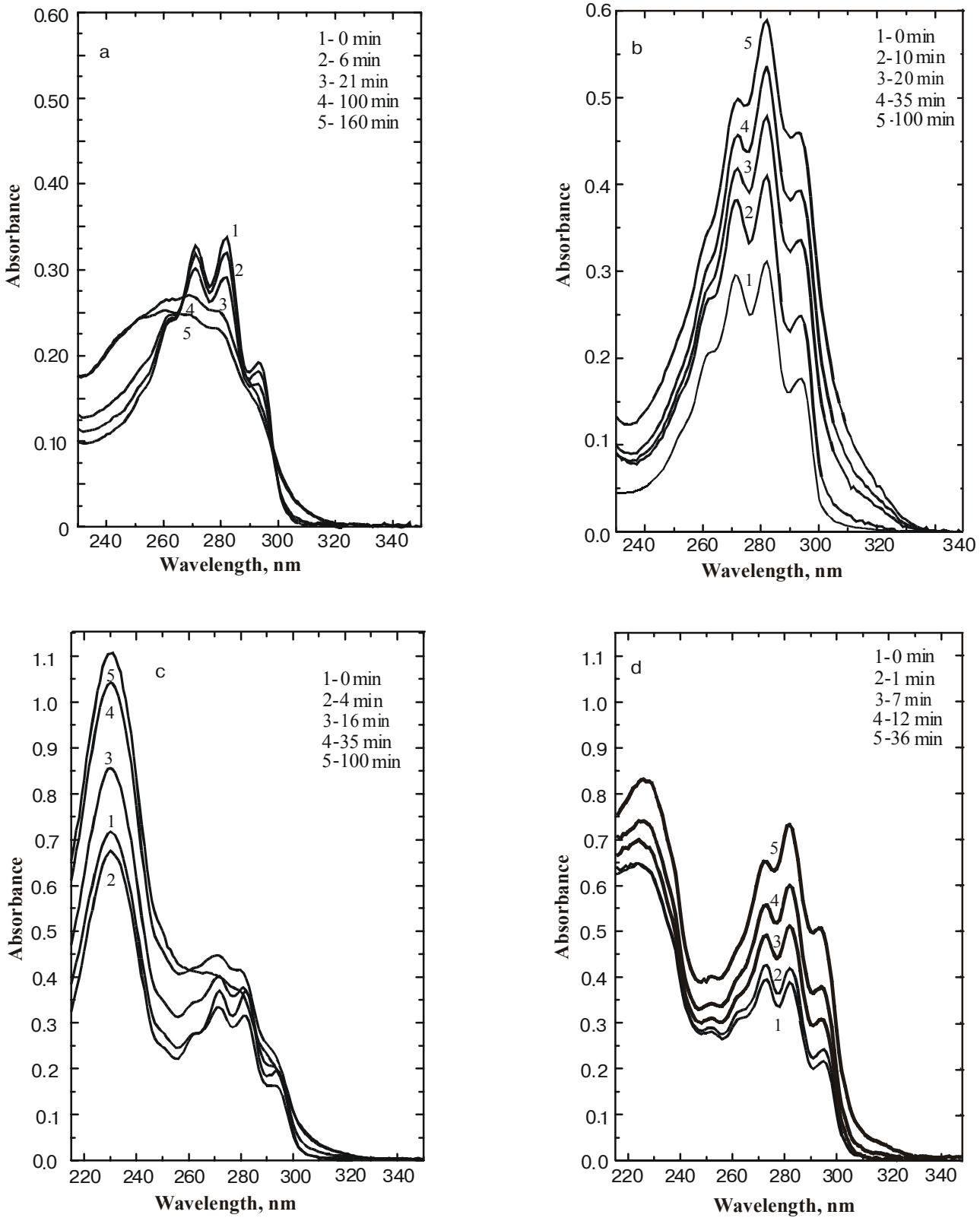

Fig.3. Spectral kinetics under irradiation with the EL-30 lamp: a) 7-DHC in ethanol, b) 7-DHC in LC matrix, c) 7-DHC-Bz in ethanol, d) 7-DHC-Bz in LC matrix.

Besides, pronounced distinction between the 7-DHC and 7-DHC-Bz spectra in the short-wave range (around 230 nm) gives an indication of additional photoreaction channel in the case of 7-DHC-Bz. For this latter it has been found that within several hours after termination of UV irradiation the absorbance at 230 nm (both in ethanol and LC matrix) returns to its original value that suggests the thermoreversibility of this photoreaction channel. This feature can be assosiated with flexibility of benzoic fragment in relation to rigid steroid sceleton of the 7-DHC-Bz molecule [11].

The results of UV irradiation of chiral nematic phase in the wedge-shape cell are presented in Fig. 4. Close correlation between the changes in the Cano stripes number and the transmittance changes is easily seen for both dopants. Moreover, as the number of the Cano stripes remains fixed with the time of UV exposure, the transmittance is changed negligibly, but the every change in N_C is accompanied by the sudden change in the transmittance that may be assosiated with the 2nd order phase transition. In spite of considerable quantitative difference between the 7-DHC and 7-DHC-Bz in the UV dose dependence, in both cases the three stages can be recognized in the course of UV irradiation. At the 1st stage the N_C increase can indicate that the orientational ordering took place due to dissipation of the excitation energy after UV absorption by the dopant molecules. At the 2nd stage it is likely that the dopant molecules in LC matrix are hold in the most unique position with minimum energy and the number of the Cano stripes is not changed with UV exposure. And at the 3rd stage the N_C decrease indicates that the chiral dopants undergo photochemical transformations and converted into isomers possessing considerably lesser HTP value as compared with the parent compounds.

Of prime importance is the reversibility effect that has been found for the LC doped with 7-DHC-Bz. Despite prolonged UV exposure resulted in total disappearance of the Cano stripes, dark storage within several hours resulted in the reappearance of the Cano texture with the original pitch value. When heated to 313 K, the restoration process was considerably accelerated, and the switching cycle was performed 7 times without deterioration of the LC phase. This special feature is useful for optical data storage and molecular memory elements.

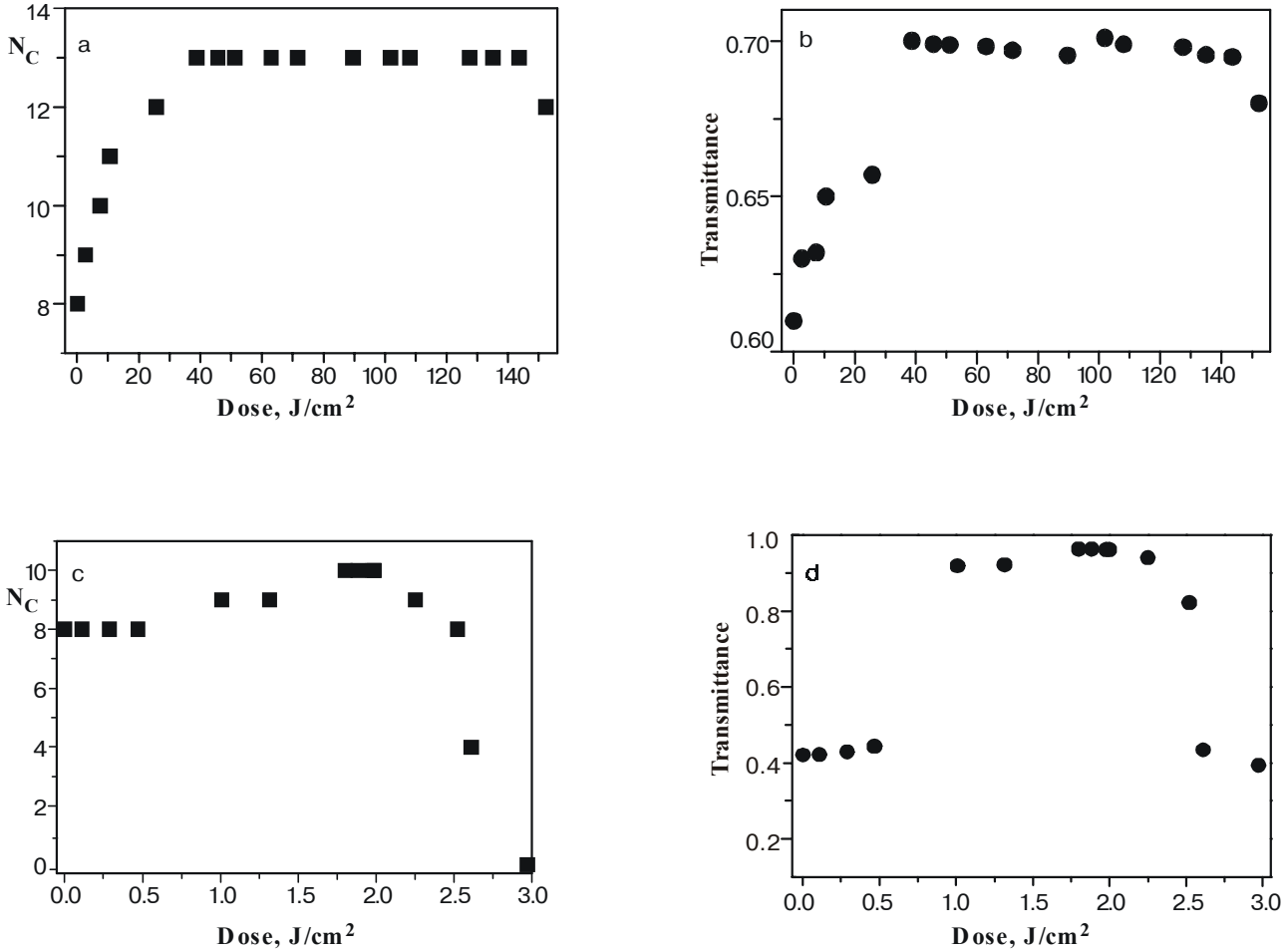

Fig.4. Dependence of the Cano stripes number (a - 7-DHC, c – 7-DHC-Bz) and the LC cell transmittance (b – 7-DHC, d – 7-DHC-Bz) on the UV dose.

Conclusions

In the first time it has been experimentally found that chiral molecules of 7-DHC and 7-DCH-Bz induce stable cholesteric phases when doped in the nematic LC. Dependence of the cholesteric pitch on the irradiation UV dose has been observed that may be exploited for UV dosimetry.

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