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### Features of Previtamin D Cis-Trans Isomerization in the Nematic LC Matrices: Orientation and Cholesteric Order Effects

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## Features of Previtamin D *Cis-Trans* Isomerization in the Nematic LC Matrices: Orientation and Cholesteric Order Effects

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*For the first time 7-dehydrocholesterol (7-DHC, provitamin D<sub>3</sub>) photoisomerization was studied in nematic LC matrices (ZLI-1695, ZhK-805) in comparison with ethanol solution using UV absorption spectroscopy. Dissolution of chiral 7-DHC molecules in the nematic LCs induces cholesteric phase, and dramatic effect of the cholesteric pitch value on the spectral kinetics has been revealed. Significant increase in trans-isomer accumulation was observed as the cholesteric pitch was reduced from 2200 to 25 mkm. Noticeable effect of the LC orientation has been observed as well.*

**Keywords:** induced cholesteric; photochemistry in organized media, provitamin D *cis-trans* isomerization, UV absorption spectroscopy

## INTRODUCTION

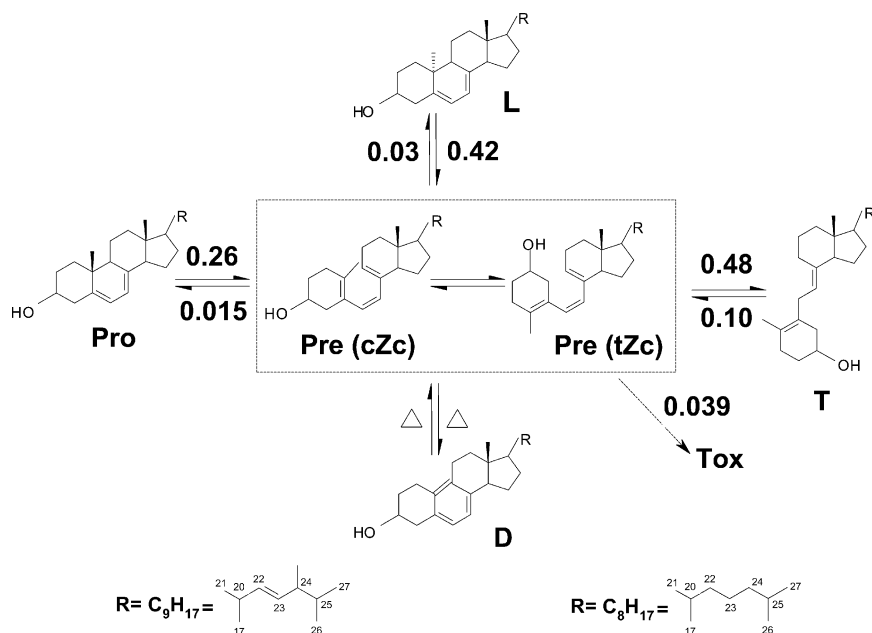
Photomodulation of orientations of liquid crystals (LCs) induced by photochemical reactions of doped photochromic molecules is of great current interest. From the other side, employment of liquid-crystalline media to explore the influence of anisotropic environments on thermal and photochemical reactions of dopant molecules has attracted considerable attention [1].

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Here we discuss the effect of LC microenvironment on the photoisomerization of 7-dehydrocholesterol (provitamin D<sub>3</sub>) that underlies the complex network of vitamin D synthesis. As is known, in solution UV irradiation of provitamin D within its absorption band (240–315 nm) yields rotationally flexible previtamin D that further undergoes side photoconversions among which *cis-trans* isomerization into tachysterol is the most efficient one ( $\phi_{cis-trans} = 0.48$ ) [2]. In view of the structural requirements, it is assumed that cZc-Pre conformers are precursors of ring-closed products whereas tZc-Pre conformers are predominantly undergo *cis-trans* photoisomerization [3,4] (Fig. 1).

Studies of provitamin D photoisomerization in heterogeneous media established pronounced effect of microenvironment on provitamin D *cis-trans* photoisomerization that is coordinated with the principle of ground state conformation control and reflects the reaction medium effect on the conformational equilibrium of provitamin D molecule [5].



**FIGURE 1** The reaction scheme of vitamin D synthesis including two planar previtamin D conformers [3]: **Pro** – provitamin D, **Pre** – previtamin D, **T** – tachysterol, **L** – lumisterol, **Tox** – toxysterols, **D** – vitamin D.  $R = C_8H_{17}$  – Vitamin D<sub>3</sub> series,  $R = C_9H_{17}$  – Vitamin D<sub>2</sub> series. Numbers with arrows represent the photoconversion quantum yields.

Significant increase of the rate constants for the previtamin D<sub>3</sub> ⇌ vitamin D<sub>3</sub> thermoreaction was observed in the cholesteric liquid-crystalline mixture in comparison with hydrocarbon solvents [6]. A possible explanation involved microscopic interactions which shifted conformational equilibrium in favor of cZc-Pre conformers that are more cholesteric-like than is tZc-Pre conformer and, therefore, may 'fit' better into the cholesteric mixture [6].

## MATERIALS AND METHODS

Irradiation of 7-dehydrocholesterol (Fluka) in ethanol ( $C \approx 10^{-4}$  mol/l) and in the LC matrices was carried out at  $t = 20^\circ\text{C}$  using the BUV-30 lamp ( $\lambda_{\text{irr}} = 254$  nm). Ethanol solution of 7-DHC was irradiated in standard quartz cuvette ( $d = 1$  cm), and the LC mixtures were irradiated in quartz cells ( $10 \times 35$  mm<sup>2</sup>) of different thickness.

Nematic LC-805 (1:1 mixture of 4-n-butyl- and 4-n-hexyl-trans-cyclohexan-1-carboxylic acids) and ZLI-1695 (Merck) have been selected as host matrices because of their transparency in the UV range (250–350 nm) and thermal stability over the interval 10–407°C. The cholesteric phase with the right-handed macrohelix was induced by doping LCs with the chiral 7-DHC molecules, and the cholesteric pitch,  $P$ , was changed within  $25 \div 2200$  mkm depending on the LC cell thickness ( $6 \div 135$  mkm) and 7-DHC concentration ( $1.73 \div 0.07$  wt %) [7].

The UV absorption spectra were recorded within 230–330 nm with the Perkin & Elmer Lambda-25 spectrophotometer before UV irradiation and after fixed UV exposures. Further to derive the photoisomer concentrations in ethanol the spectra were processed with computer according to the original program that used known individual spectra of the photoisomers in solution as the reference ones [8]. However, the spectrophotometric analysis of the LC samples was impeded because of small shift and distortion of the 7-DHC spectrum in the LC matrices. Nevertheless, HPLC analysis of 7-DHC photoisomerization in the LC matrices [6,9] showed that the same photoproducts were formed as in solution.

In ethanol under irradiation at 254 nm *trans*-isomer tachysterol is formed in high concentration ( $\sim 70\%$ ) and its accumulation results in the remarkable increase of the maximum absorbance at 282 nm till the quasi-photostationary state is established [10]. Then this increase stops and under further irradiation the absorbance gradually decreases due to the irreversible photoreactions.

That is why the maximum absorbance increase can serve as an indirect measure of *trans*-isomer amount in the photoisomer mixture (on the condition that slow rates of the irreversible photoreactions remain unalterable in the LC matrix).

## RESULTS AND DISCUSSION

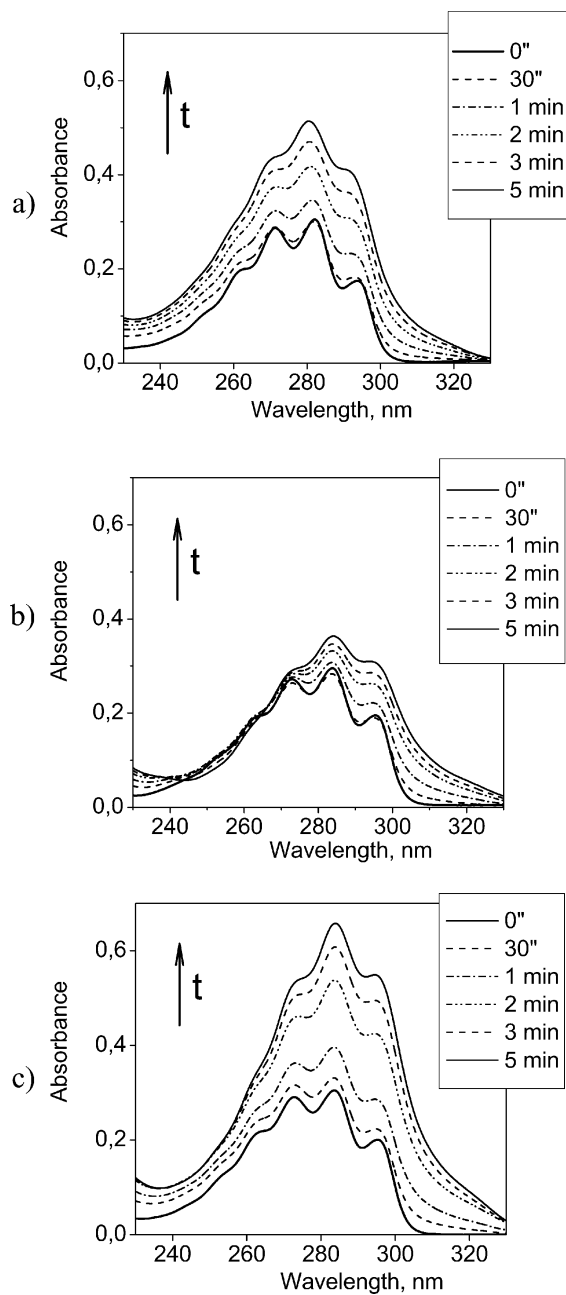
A number of the LC samples of different thickness but with the same initial optical density were irradiated, and the absorption spectra transformations under UV irradiation were recorded and compared with those ones in ethanol (Fig. 2). It was observed that in the thick LC cell ( $L = 135 \text{ mkm}$ ) the maximum absorbance increased in lesser degree than in ethanol (Fig. 2a, b). However, this increase significantly ascended in the more thin LC cells (Fig. 2c). At the same time under prolonged UV irradiation the absorbance gradual descent in all the LC samples was slower than in ethanol indicating the irreversible photoreactions retardation (Fig. 3).

Dramatic effect of the cholesteric pitch value on the maximum absorbance increase is clearly shown in Figure 4 where a dotted-line indicates this value in ethanol.

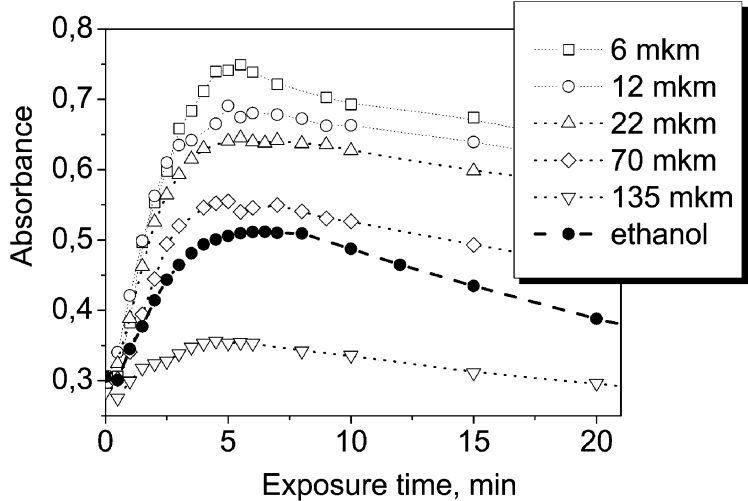
Noticeable effect of the LC orientation on the absorbance behavior was observed as well. As compared with a non-oriented LC sample, the maximum absorbance elevation was remarkably higher (15%) for the planar oriented LC cells in which the substrates were coated with a polydimethylsiloxane (PDMS) alignment layer.

Additional experiment was undertaken with the LC cells of  $135 \text{ mkm}$  thickness assembled with the PDMS coated substrates for elucidation of the twist effect on the photoreaction kinetics. In this case three samples were irradiated: the  $90^\circ$  left-twisted one, the untwisted one and the  $90^\circ$  right-twisted one. The time-dependences of maximum absorbance shown in Figure 5 clearly demonstrate that the right-side twist induced the maximum absorbance increase in comparison with the untwisted one as opposed to the left-side twist. These data on the artificial twisting and untwisting of the cholesteric macrohelix also confirm extremely high sensitivity of the spectral kinetics to the cholesteric pitch value.

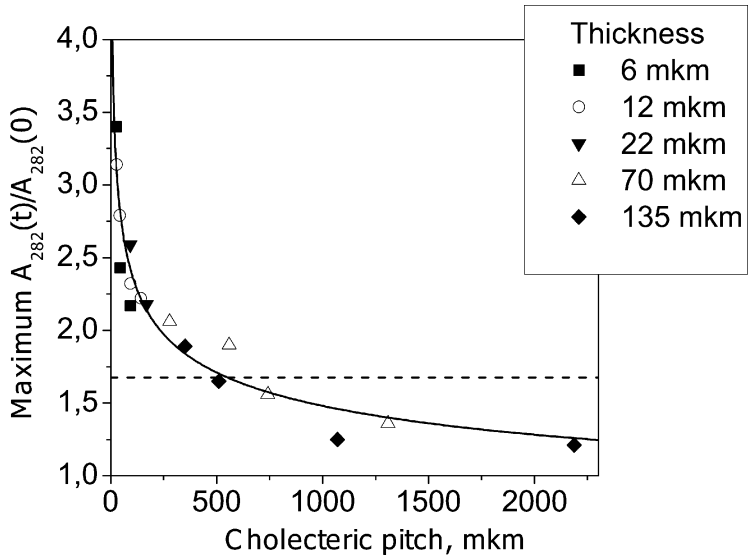
According to the Bouguer's law the absorbance increase might result from both the increase of the *trans*-isomer extinction coefficient  $\varepsilon$  and/or its concentration. Moreover, certain correlations between conformation and spectroscopic data are well known: when the nuclear geometry of a chromophore in the ground state is made more planar, the absorption spectrum becomes more structured and red shifted, and the values of  $\varepsilon$  become larger [11]. Just the observed  $1 \text{ nm}$  red shift of the 7-DHC absorption spectrum in the LC matrix which increases up to  $4 \text{ nm}$  during irradiation suggests that due to specific interaction of tachysterol molecule with the microenvironment its nuclear conformation becomes more planar and linear in comparison with ethanol solution.



**FIGURE 2** Transformation of the 7-DHC initial absorption spectrum as a result of UV irradiation at 254 nm: in ethanol (a), in the LC cells of thickness  $L = 135$  mkm (b) and  $L = 22$  mkm (c).

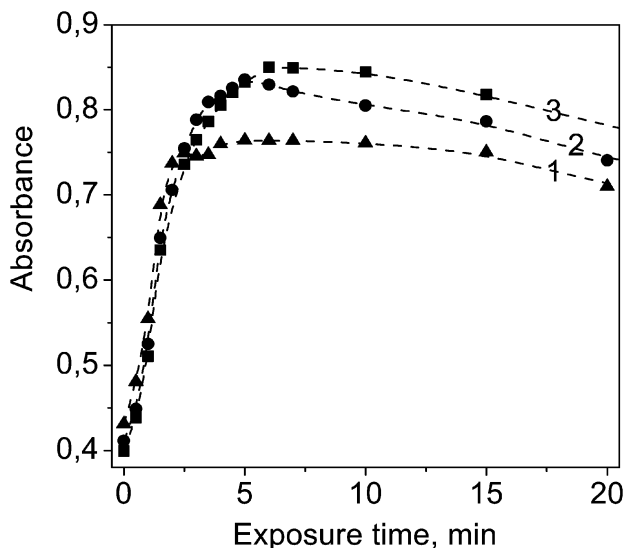


**FIGURE 3** Evolution of the absorbance at 282 nm with the exposure time in the LC cells of different thickness (ZLI-1695) in comparison with ethanol (solid symbols).



**FIGURE 4** Dependence of relative maximum absorbance increase in the LC matrix (ZLI-1695) on the cholesteric pitch value. Dotted line shows the maximum increase in ethanol.





**FIGURE 5** Evolution of the absorbance at  $\lambda = 282$  nm with the exposure time in the left-twisted (curve 1), untwisted (curve 2) and right-twisted (curve 3) LC cells of 135 mkm thickness with the same concentration of 7-DHC ( $C = 0.1$  wt%). For the untwisted cell the cholesteric pitch  $P = 765.5$  mkm.

From the other side, the increase of tachysterol concentration due to more efficient *cis-trans* photoisomerization of previtamin D in the LC matrix may also account for the absorbance growth. However, the increase of the *cis-trans* isomerization quantum yield in more viscous LC medium is hardly understandable considering its classic mechanism of the one-half molecule rotation around the  $C=C$  double bond. We suggest that the layer structure of the nematic LC is more favorable for sliding motion of the two halves of the molecule between the layers in the plane of the triene  $\pi$ -system.

Therefore we speculate that most likely in the LC matrix a volume-conserving 'Hula-Twist' mechanism of *cis-trans* isomerisation [12] becomes the dominant process when classic torsional relaxation is prohibited in view of the free-volume restrictions.

## CONCLUSIONS

Substantial difference in the spectral kinetics of provitamin D<sub>3</sub> photoisomerization in the nematic LC matrices has been revealed as compared with ethanol solution. Remarkable effect of the LC orientation was observed in parallel with dramatic effect of the cholesteric pitch

value. We hypothesize that specific ordering and solvent-solute spatial interactions in the induced cholesteric LC may be responsible for the increasing amount of the rod-like *trans*-isomer conformers that possess the least helical twisting power.

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