Institute of Cybernetics
Georgian Academy of Sciences
Tbilisi, Sandro Euli str. 5

Proceedings of the
Institute of Cybernetics
Vol. 3, N1-2, 2004

COLOUR CHANGE EFFECT BASED ON PROVITAMIN D PHOTOTRANSFORMATION IN RIGHT AND LEFT-HANDED CHOLESTERIC LIQUID CRYSTALLINE MIXTURES

M. ARONISHIDZE, A. CHANISHVILI, G. CHILAYA, G. PETRIASHVILI; S. TAVZARASHVILI, L. LISETSKI, N.KIREYEVA , I. GVOZDOVSKYY, I.TERENETSKAYA

ABSTRACT. It has been shown that UV radiation can produce observable color changes in induced cholesteric systems (nematic + optically active dopant) additionally doped with ergosterol (provitamin D_2). The effect is based on the photoinduced conversion of ergosterol into vitamin D_2, which has the opposite sign of its helical twisting power. For better understanding of the phototransformation mechanism, the cholesteric systems were also doped with vitamin D_2. The observed shifts of the selective reflection peaks (more than 30 nm after 10 min of UV irradiation) allow both instrumental and visual monitoring of biologically active UV radiation.

Introduction. The cholesteric mesophase is an excellent medium sensitive to the smallest changes in molecular structure [1]-[3]. Photo-optical effects in absorbing liquid crystals (LC) have been studied mostly in systems where the chemical structure or conformation of the constituent molecules is changed by irradiation. A colour shift in induced cholesteric LC systems (mixtures of an achiral LC with an optically active mesomorphic or non-mesomorphic dopant) [4]-[6] was observed when a conformationally active dye was added to a cholesteric liquid crystal [7], or when a photoisomerizable chiral compound was used as a chiral dopant [8]-[11], or when of a photoisomerizable nematic component was used in induced cholesteric mixtures [12]-[13].

In this work we continue the realization of a new idea [14]-[15]: the use of vitamin D derivatives as chiral dopants in induced cholesteric structures. This approach is very promising for a new application of liquid crystals – development of photosensitive cholesteric mixtures controlled by the solar UV irradiation [14]-[16].

Materials and methods. The induced cholesteric liquid crystals used in our study should have a broad temperature range of the mesophase. It is important for the UV biosensor that its helical pitch should be temperature independent (or weakly dependent). Moreover, the cholesteric mixture used should be composed of a nematic host and a chiral dopant, both non-photoisomerizable and transparent in the visible and near-UV ranges.

As it can be seen from Fig.1, the most suitable nematic components from the viewpoint of their UV transparency are cyclohexyl cyclohexanes.

Thus, we selected the nematic mixture $ZLI-1695$ (Merck) as our nematic host, which is the mixture of cyclohexyl cyclohexanes

R = C_2, C_3, C_4, $C_7$with nematic range 13-72 $^\circ$C.

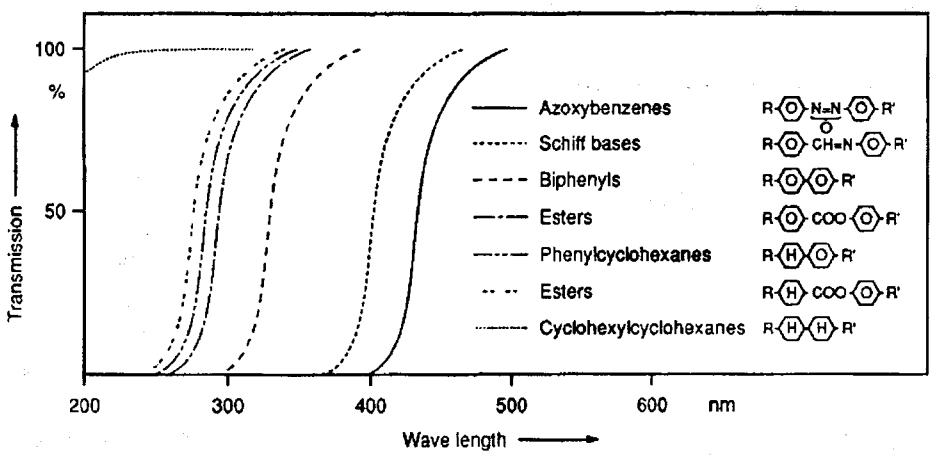
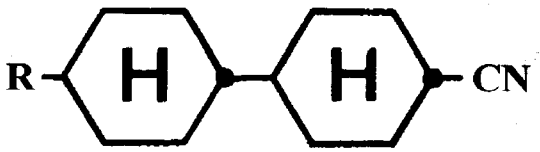
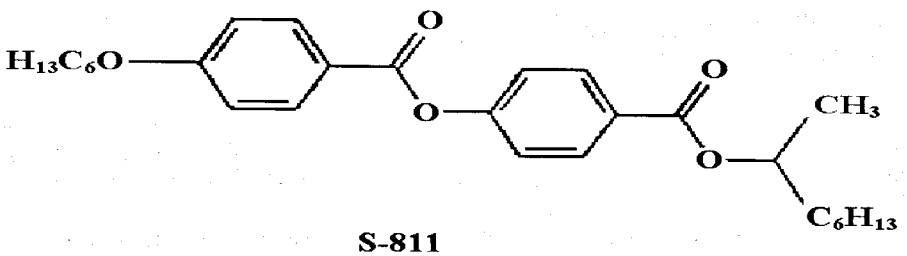


FIGURE 1. Absorption edge of liquid crystals (layer thickness = 10μm) [17].



As chiral dopants, we used left-handed $ZLI-811$ $(S-811)$ and right-handed $ZLI-3786$ $(R-811)$. The molar mass for both dopants $M = 454.6$ g·mole^{-1}, melting point 48 ° C, rotatory power (HTP) - $[\alpha]^{20}_{D,CHCl3} = \pm 26\,^{\circ}$ dm$^{-1}\cdot$ (g/ml)$^{-1}$;



S-811

The absorption spectrum of 1% solution of $S-811$ in $ZLI-1695$ is shown in Figure2.

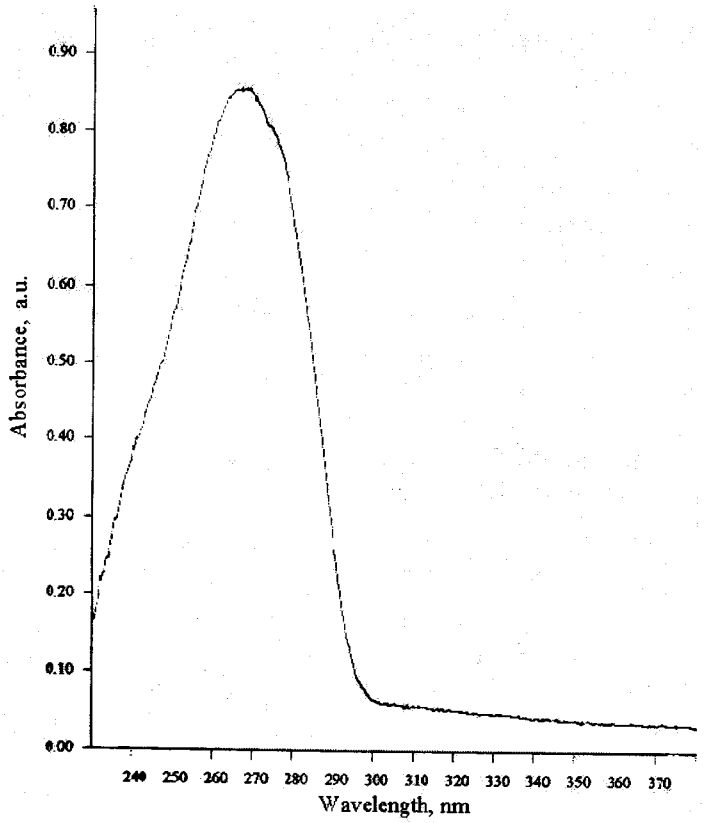


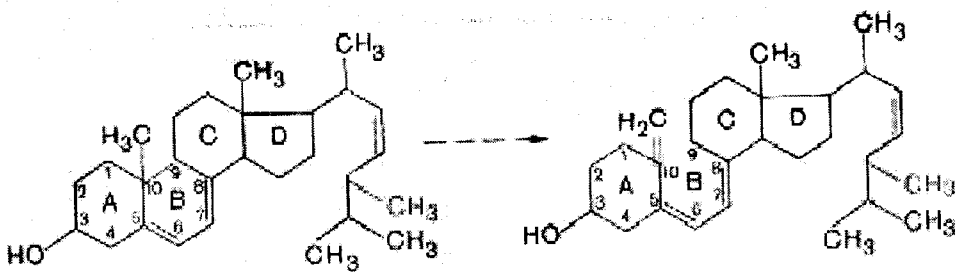
FIGURE 2. Absorption spectrum of 1% solution of $S-811$ in $ZLI1695$.

As it is known, under UV irradiation provitamin D is converted, via intermediate photoconversion stages [1] , into vitamin D[18]-[19].

As it can be seen from the scheme, vitamin D_2 is formed from ergosterol as a result of breaking of the chemical bond between the 9th and 10th carbon atoms in the ring B, which occurs under UV irradiation.

Provitamin D_2 (ergosterol) induces right-handed helical twisting in nematic liquid crystals. while the helix induced by vitamin D_2 is left-handed [20]. Unfortunately. the helical twisting power of compounds from the vitamin D group is too small for induction of a cholesteric structure with helical pitch values ensuring selective reflection in the visible range [20]. Therefore, our first idea of the liquid-crystalline UV biosensor consisted in the use of a wedge-like LC cell filled with the

[1] The terminology "vitamin D" is employed here in general sense, as two principal chemical species of this kind are available. Vitamins D_2, or ergocalciferol ($C_{28}H_{44}O$) and D_3, or cholecalciferol ($C_{27}H_{44}O$) are produced from their precursors ergosterol and 7-dehydrocholesterol (7-DHC), respectively.



ergosterol (provitamin D_2) vitamin D_2

two-component mixture (NLC + provitamin D). In this case the reduction of the number of Cano stripes should be proportional to the absorbed UV dose [14]-[16].

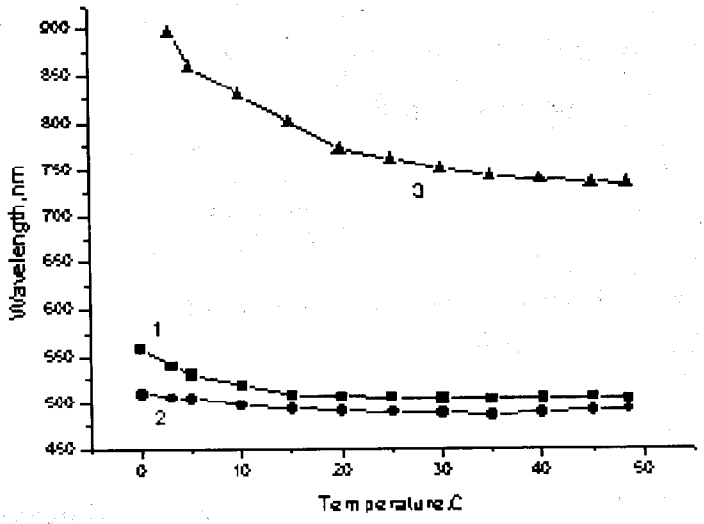


FIGURE 3. Temperature dependence of the selective reflection peak for mixtures: 1 - 73%ZLI-1695 + 27%ZLI-811R; 2 - 92%(73%ZLI-1695 + 27%ZLI-811R) + 8%ProD$_2$; 3 - 92%(73%ZLI-1695 + 27%ZLI-811R) + 8%D$_2$

Our next idea was to add one of the substances of the vitamin D group – provitamin D_2, or ergosterol - to a cholesteric mixture already possessing its pitch in the visible range [21]-[24]. In these experiments, we doped right- and left-handed cholesterics with provitamin D_2 and recorded the resulting color changes (i.e., the helical pitch variation) due to photoisomerization of provitamin D_2. To check the

general course of the phototransformation reaction, we also doped the cholesteric compositions with vitamin D_2 under the same conditions. Ergosterol and vitamin D_2 used in our experiments were obtained from Sigma.

The experimental studies were carried out using a standard sandwich-type cell (thickness ~ 10 μm). The transmission spectra measurements were made at room temperature using a Specord M40 spectrophotometer. A 100W medium pressure mercury lamp and a filter transparent in the wavelength range 290-400 nm were used in our UV irradiation setup.

Results and discussion. Depending on the handedness of the initial cholesteric structure, the pitch, after doping by ergosterol or vitamin D_2, can either increase or decrease (Figs 3, 4).

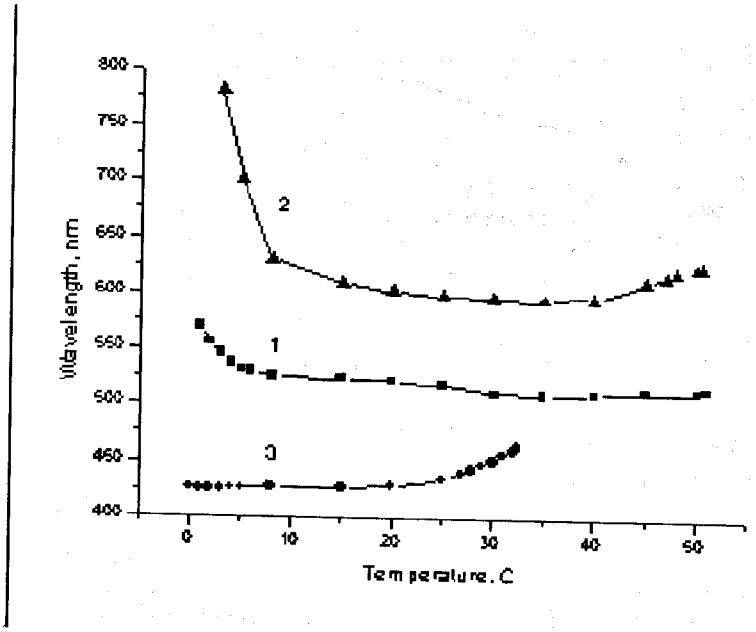


FIGURE 4. Temperature dependence of selective reflection peak for mixtures: 1 - 73%ZLI-1695 + 27%ZLI-811S; 2 - 92 %(73%ZLI-1695 + 27%ZLI-811S) + 8%ProD_2; 3 - 92 %(73%ZLI-1695 + 27%ZLI-811S) + 8%D_2.

Under UV irradiation, as a result of photo transformation of ergosterol, the pitch changed in the opposite direction, i.e., back to the pitch values for the initial (undoped) cholesteric structure and further on (Figs. 5 and 6). This is in agreement with the data on the effective helical twisting sense of vitamin D_2, known to be opposite to that of ergosterol [19].

We also studied changes in the selective reflection peak position after irradiation had stopped. As shown in Figs. 5 and 6, the selective reflection peak is continued

to be shifted further on. This fact indicates that not all molecules of provitamin D_2 are transformed to vitamin D_2 during irradiation. This is also in agreement with the experimental fact that just by means of UV-induced transformation we cannot reach the selective reflection peak values obtained by doping the cholesteric matrix with vitamin D_2. A similar behaviour was earlier observed with another cholesteric matrix [24].

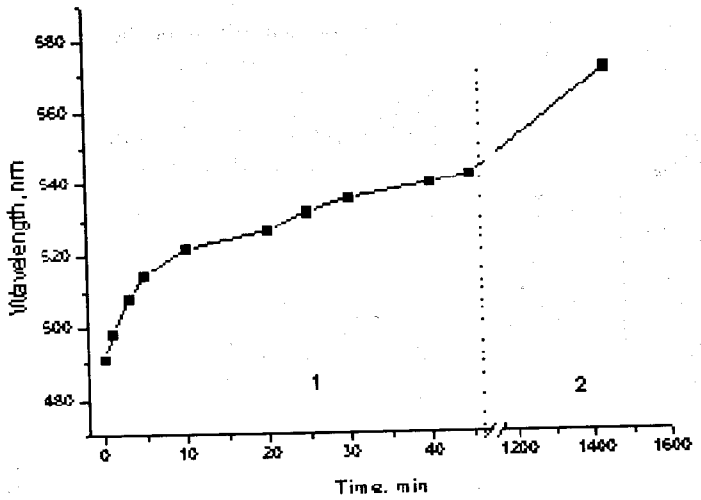


FIGURE 5. Exposure time dependence for mixture: 92%(73%ZLI-1695 + 27%ZLI-811R) + 8%ProD_2.

The values of the selective reflection peak changes with UV exposure (the colour change) were different in case of the two cholesteric matrices (Fig.5 and Fig.6). In the first case, a pronounced colour change ($\sim$ 25 nm shift) was observed as a result of 2 min exposure (Fig.6), but in the other case, the colour change ($\sim$ 30 nm shift) was observed after 10 min exposure (Fig.5).

Conclusions. 1. We have shown a possibility of UVB radiation (280-315nm) detection by monitoring the helical pitch changes caused by the photo induced transformation of provitamin D_2 to vitamin D_2 in the cholesteric matrix.

2. The developed cholesteric sensor material, comprising a nematic LC mixture, a UV-insensitive chiral dopant and 8-10% of ergosterol, displayed shifts of the selective reflection peaks by up to 25-30 nm after 2-10 min of UV irradiation, making possible both instrumental and visual (by color change) monitoring of UVB radiation.

Acknowledgements. We are thankful to Merck for supplying liquid crystal materials and chiral dopants. The work was supported by the STCU Project N GG-50(j).

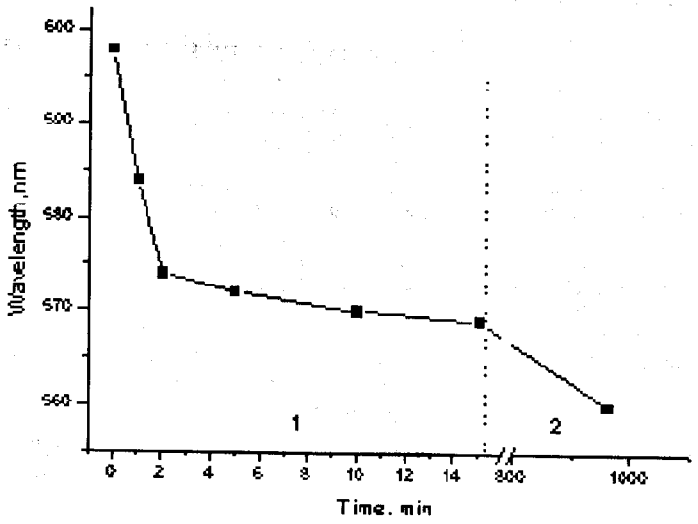


FIGURE 6. Exposure time dependence for mixture: 92 %(73%ZLI-1695 + 27%ZLI-811S) + 8%ProD$_2$

REFERENCES

[1] G.Chilaya, Cholesteric Liquid Crystals: Optics, Electrooptics and Photooptics, in: Chirality in Liquid Crystals, H.-S. Kitzerow and Ch.Bahr, eds. (series Partially Ordered Systems, Springer Verlag, New York, 2001), Chapter 6, pp 159-185.

[2] G.S.Chilaya, "Effect of various external factors and pretransitional phenomena on structural transformations in cholesteric liquid crystals",Crystallography Reports, V.45, 871-886 (2000); [Kristallografiya V.45, 944-960 (2000)]

[3] B.L.Feringa, R.A.van Delden, N.Koumura, E.M.Geertsema, "Chirooptical molecular switches", Chem.Rev., V.100, 1789-1816, (2000).

[4] G.Chilaya, "Induction of chirality in nematic phases", Rev. Phys.Appliq. V.16, 193-208 (1981).

[5] G.S.Chilaya and L.N.Lisetski, "Helical Twist in Cholesreric Mesophases", Sov.Phys.Usp. V.24, 496-510 (1981).

[6] G.S.Chilaya and L.N.Lisetski,"Cholesteric liquid crystals: physical properties and molecular -statistical theories", Mol.Cryst.Liq.Cryst., V.140, 243-286 (1986).

[7] E.Sackman, "Photochemically induced reversible colour changes in cholesteric liquid crystals", J. Am. Chem. Soc., V.93, 7088-7090 (1971).

[8] V.Vinogradov, A.Khizhniak, L.Kutulya, Yu.Reznikov, V.Reshetnyak, "Photoinduced change of cholesteric LC-pitch, Mol.Cryst.Liq.Cryst. V.192, 273-278 (1990).

[9] A.Yu. Bobrowski, N.I.Boiko, V.P.Shibaev, "New chiral photochromic menthone-containing homopolymers and copolymers - synthesis, phase behavior and photo-optical properties", Liquid Crystals, V.26, 1749-1765 (1999).

[10] P. van de Witte, M.Brehmer, J. Lub, "LCD components obtained by patterning o chiral nematic polymer layers", J.Mater.Chem. V.9, pp.2087-2094 (1999).

[11] F.Vicentini, J.Cho, L.-C.Chien", Tuneable chiral materials for multicolour reflective cholesteric displays", Liquid Crystals, V.24, pp.483-488 (1998).
[12] A. Chanishvili, G. Chilaya, G. Petriashvili, D. Sikharulidze, Light induced effects in absorbing cholesterics, 6th European conference on Liquid Crystals, 2001, Halle (Germany), abstracts # 2-P3.
[13] A. Chanishvili, G. Chilaya, G. Petriashvili, D. Sikharulidze, "Light induced effects in cholesteric mixtures with a photosensitive nematic host," Mol. Cryst. Liq. Cryst (to be published)
[14] I.Terenetskaya, I. Gvozdovsky, Development of personal UV biodosimeter based on vitamin D photosynthesis, Mol.Cryst. & Liq.Cryst. V.368, 551-558 (2001).
[15] .Terenetskaya, I.Gvozdovskyy "Biological activity of solar UV-B radiation: A new biosensor of vitamin D synthetic capacity", SPIE Proceedings, V.4425 (2001) pp.183-188.
[16] I.Gvozdovskyy, I.Terenetskaya, "Development of personal UVB biosensor: detection of previtamin D photosynthesis", in: "Biologic Effects of Light 2001", Proceedings of a Symposium, Boston, USA, June 16-18, 2001, M.F.Holick, Ed. Kluver Academic Publishers, 2002, Boston, pp.341-353.
[17] L.Pohl, "Application in Liquid Crystals in Spectroscopy", in "Liquid Crystals", H.Stegemeyer, Guest Ed.-Steinkopff Darmstadt, New York: Springer, 1994, chapter 5, pp. 173-193.
[18] T.T.Berezov, B.F.Korovkin, Biological Chemistry, Moscow, "Medicina", 1990 (in Russ.)
[19] A.C.Mayer, A.W.Norman, Vitamin D, in: Encyclopedia of Human Biology, Vol.7, Academic Press, New York, 1991, pp.859-871.
[20] I.Gvozdovskyy and I Terenetskaya, "Steroid motor: dynamics of cholesteric helix induction in the nematic droplet", Liquid Crystals Today, V.11, pp. 8-12 (2002).
[21] O.V.Korzovska, I.P.Terenetskaya, L.N.Lisetski, "On a possibility to monitor the vitamin D formation processes using selective reflection properties of cholesteric liquid crystals", Biophysical Bulletin (Proc.Kharkiv Univ., No.488), No.1, pp. 71-74 (2000).
[22] M.Aronishidze, A.Chanishvili, G. Chilaya, G.Petriashvili; S.Tavzarashvili, L.Lisetski, I.Gvozdovskyy, I.Terenetskaya, "Colour change effect based on provitamin D phototransformation in cholesteric liquid crystal mixtures", Abstracts of 7^{th} European Conference on Liquid Crystals, Jaca, Spain, 6-11 April 2003, O26.
[23] M.Aronishidze, A.Chanishvili, G. Chilaya, G.Petriashvili; S.Tavzarashvili, L.Lisetski, I.Gvozdovskyy, I.Terenetskaya, "Colour change effect based on provitamin D phototransformation in cholesteric liquid crystal mixtures", Mol.Cryst.Liq.Cryst. (in press).
[24] L.N.Lisetski, N.A.Kireyeva, V.D.Panikarskaya, O.V.Vashchenko, G.S.Chilaya, I.P.Terenetskaya, "Cholesteric liquid crystals as sensor materials for bioequivalent UV-dosimetry", Zhidkie kristally i ikh prakticheskoe primenenie (Liquid Crystals and their Applications), Ed. Sodruzhestvo ILC Society and Ivanovo State University, Ivanovo, Russia, v.3, No.1, p.54-59 (2003).

Authors addresses:
0186, Sandro Euli, st.5, Tbilisi, Georgia
Institute of Cybernetics
Georgian Academy of Sciences

Institute for Single Crystals,
NAS of Ukraine, Kharkov, Ukraine

Institute of Physics,
NAS of Ukraine, Kiev, Ukraine