Gvozdovskyy I.A. UV-induced effects in the nematic liquid crystals with dopants of the steroid biomolecules. – Manuscript.

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As is known, steroid compounds possess properties of cholesteric liquid crystals (LCs) in narrow temperature range in the vicinity of melting point, and the cholesteric pitch is strongly affected by the structure of alifatic groups as well as position of the double bonds in the steroid ring system. In this thesis it has been found that the cholesteric phase is induced in the nematic liquid crystals (ZhK-805 and ZLI-1695) by steroid biomolecules (vitamin D isomers and relative compounds) as chiral dopants. To obtain the cholesteric phase the steroid substance was dissolved in nematic LC, and typical “fingerprint” texture was observed with polarized microscope. The value of the cholesteric pitch and the sign of cholesteric helix were measured by the Cano-Grandjean method using a wedge-like LC cell. It has been observed that dopants with rigid steroid skeleton (cholesterol, 7-dehydrocholesterol, lumisterol and ergosterol) possess lower helix twisting power (HTP) in contrast to steroid with flexible molecular structure of vitamin D (ergocalciferol). Interestingly, almost identical cholesteric pitch values about 9÷10μm were found for all the compounds (at concentration of chiral dopants C =10 wt.%) except vitamin D_2 which induced helix of 3÷4μm pitch length. In all cases the cholesteric helixes were left-handed except provitamins D_3 and D_2 (7-dechydrocholesterol and ergosterol) which induced right-handed helix. It is remarkable that substitution of peripheric OH-group in the C_3-position by benzoic acid led to the change in the helix sign in case of 7-DHC but had no effect in case of cholesterol.

For the first time dynamic of the cholesteric phase induction was studied by observation the dissolution process of a steroid microcrystal of 0.1÷1mm length at the nematic droplet. Using a polarizing microscope, the new effect of rotation of a needle-shaped or prismoidal microcrystals was observed during dissolution in the nematic droplet. It is particularly remarkable that for all the compounds the correlation between the rotation direction and the sign of the induced cholesteric helix was observed. Namely, for 7-dehydrocholesterol and ergosterol, which induced right-handed helix, the rotation in the clockwise direction was observed, whereas for the other steroids, which induced left handed helix the rotation was in the counter-clockwise direction. It is significant that no rotation of the steroid crystals was observed in the isotropic solvent or isotropic phase of LCs.

In the 2nd chapter the effects of UV irradiation on the induced cholesteric phase were studied. It is known that provitamin D under UV irradiation within its absorption band (230÷330nm) is converted into previtamin D by hexadiene ring opening. In its turn previtamin D undergoes a number of side photoconversions, and *cis-trans* isomerization into tachysterol is the most efficient one ($\varphi_{cis\text{-}trans}$ = 0.48).

During UV irradiation at 254nm the *trans*-isomer is accumulated in high concentration (up to 70%) that is accompanied by the increase in the solution absorbance because of tachysterol high extinction. By simultaneous irradiation of provitamin D in ethanol and in the LC matrices (ZhK-805, ZLI-1695) with BUV-60 (or EL-30) lamp significant difference in the spectral kinetics has been revealed. Dramatic increase in the absorbance suggests that the *trans*-isomer tachysterol is formed more efficiently in the LC matrix. This increase in the *cis-trans* isomerization in more viscous LC medium is hardly understandable from a point of view of classic mechanism involving intramolecular rotation of one-half of the molecule around the C-C double bond. Hence, the result obtained supports the volume-conserving "Hula-Twist" mechanism proposed recently by Liu et al., which becomes dominant when classic torsional relaxation is prohibited. (The “Hula-Twist” involves simultaneous rotation (180^0) of two connected single and double bonds and simultaneous sliding motion of the two halves of the molecule in the plane of the triene π-system).

When the wedge-like LC cells with the cholesteric mixtures were irradiated with fluorescent lamp (EL-30), a progressive decrease in the Cano-Grandjean stripes number with exposure time was observed. This indicates that the chiral dopant undergoes phototransformation (hexadiene ring-opening) into a photoisomer possessing lesser HTP. Linear correlation between the decrease in the Cano stripes number and accumulation of previtamin D (*in vitro*) has been observed under simultaneous solar irradiation of the LC cell and the cuvette with ethanol solution of 7-DHC. By this means our findings hold promise for dosimetry of biologically active UV-B solar/artificial radiation (280÷315nm) by observation the Cano stripes number depending on the accumulated UV dose.

In the 3rd chapter the LCs photoalignment using thin films of the steroid biomolecules was examined. To date a number of nonrubbing techniques that are based on the photoinduced anisotropy of photosensitive organic films have been developed to produce planar or homeotropic alignment of LCs. The photoalignment ability both of the provitamin D_3-doped polymer film using polymethylmethacrylate (PMMA) and the monolayers of provitamin D_3 adsorbed (or deposited by Langmuir-Blodgett techniques) at the substrate surfaces of a LC cell was studied in the thesis.

The photoalignment ability of the polymer film was studied depending on the concentration ratio 7-DHC/PMMA, UV exposure and temperature. Effective photoalignment with maximum twist angle 43.5^0 has been observed for the ZLI 4801.000 in case of the 8:1 weight ratio 7-DHC/PMMA and the UV lamp irradiation with linearly polarized light during 15min. In this case azimuthal anchoring energy $W_\theta=1.6\cdot10^{-6}$ J/m^2 has been determined using the twist-cell method. It should be noted that in all cases the light-induced orientation axis is parallel to the polarization of the incident UV light. However it has been found that the LC orientation is temperature unstable, that means it was not restored after the LC cell heating up to120^0C and further cooling to room temperature.

In addition the LCs orientation was examined using adsorption of provitamin D_3 molecules or deposition of Langmuir-Blodgett film at the substrate surface of a LC cell. It was found that both films provide homeotropic (H) orientation of nematic LCs with negative ($\Delta\varepsilon < 0$) and positive ($\Delta\varepsilon > 0$) dielectric anisotropy. The packing density (area per molecule) of 65Å^2 was obtained for 7-DHC molecule from the π-A diagram. Upon prolonged UV exposure (up to 60 min) the transition from homeotropic to planar orientation has been observed in both nematics ($\Delta\varepsilon < 0$, $\Delta\varepsilon > 0$). Using these films, a possibility of electrically controlled change in the LC orientation was studied. Transmission-Voltage characteristics of both non-irradiated (H orientation) and irradiated (P orientation) parts of the cell with nematic LCs were measured and reversible switching between the two orientations have been achieved by applied electric field (2÷4V) that is usable for high contrast of the pixels in the LC display technology.

Key words: liquid crystal, induced cholesteric phase, steroids, isomers of vitamin D, dosimetry of UVB radiation, photoalignment.