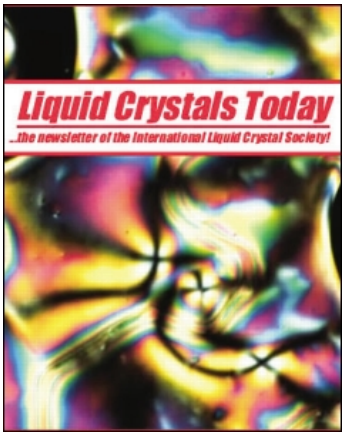

Liquid Crystals Today
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713681230

Steroid motor: dynamics of cholesteric helix induction in the nematic droplet

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Online publication date: 03 December 2010

To cite this Article Gvozdovskyy, I. and Terenetskaya, I.(2002) 'Steroid motor: dynamics of cholesteric helix induction in the nematic droplet', Liquid Crystals Today, 11: 4, 8 — 12
To link to this Article: DOI: 10.1080/146451802100006824
URL: http://dx.doi.org/10.1080/146451802100006824

Liquid Crystals Today, 2002, Vol. 11, No. 4, 8–12

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Steroid motor: dynamics of cholesteric helix induction in the nematic droplet

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A nematic liquid crystal can be converted into a cholesteric phase by a chiral dopant, and the cholesteric pitch can be changed by its photochemical transformations [1]. For the first time we investigate the dynamics of the cholesteric phase induction using seven steroids (vitamin D isomers and related compounds) as chiral dopants. Here we report the new effect of rotation of a rod-like steroid crystal (0.1–1 mm length) when it is placed at the surface of a nematic drop and its dissolution course was followed with a polarizing microscope. For all the compounds univocal correspondence was noticed between the crystal rotation direction, the helicity of the molecular steroid ring system [2] and the sign of the cholesteric macrohelix determined by the Cano–Grandjean method [3]. No rotation was observed in the isotropic phase.

Frequently, optically active molecules that possess cholesteric phases have a steroid ring system and the sign and magnitude of the cholesteric pitch are strongly dependent on the molecular conformation of the steroid moiety [4, 5]. The latter can be altered by a change in the position(s) of the double bond(s) in the steroid ring system, the effective length of the peripheral 3β group, or the structure of the 17β side-chain [4].

To investigate to what degree the above-mentioned structural alterations affect the molecular twisting power, we tested seven steroid compounds, possessing various structures, as chiral dopants in the nematic liquid-crystalline matrices (see table 1). We were guided by the following reasoning in our choice of the steroid molecules.

Cholesterol and 7-dehydrocholesterol (7-DHC, provitamin D_3) vary in the number of double bonds in the central ring B. Both of them form a cholesteric phase with a right-handed helix but of different pitch values (it is almost 3 times smaller in the case of cholesterol) [4]. Substitution of the 3β OH group in these two compounds with benzoic acid caused a change in the sign of the helix and a decrease in the cholesteric pitch [4]. However, a more significant reduction of the pitch in the case of 7-DHC benzoate caused its left-handed helix to become more twisted compared to that of cholesterol benzoate [4]. It is interesting that ergosterol (provitamin D_2), in which the 17β side-chain is little different from that in 7-DHC, does not form a cholesteric phase, and only a smectic phase of ergosterol is obtained [6].

Lumisterol$_3$ has been chosen as a diastereomer of 7-DHC [2] that also has two conjugated double bonds in ring B, but the 10-methyl group and the 9-hydrogen atom are situated on different sides as compared to 7-DHC.

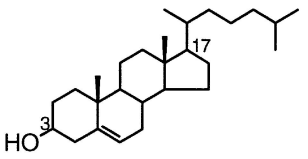
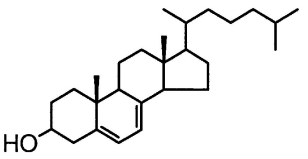
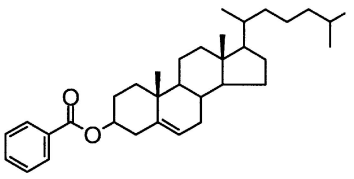
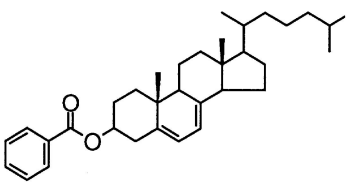
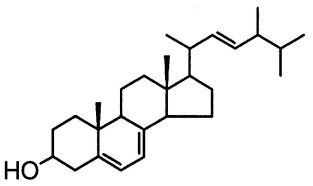
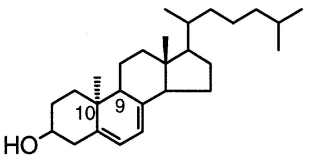
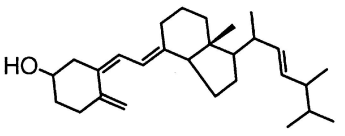
Ergocalciferol (vitamin D_2) has been chosen as the only compound with a disrupted ring B and a conjugated triene system. It was interesting to check the extent to which possible flexibility would affect the twisting power.

As nematic matrices we chose two liquid-crystalline materials: ZLI-1695 (Merck) and ZhK-805 (NIOPIK), which had previously been extensively studied in the design of our own UV biodosimeter [7]. Both materials are nematic at room temperature but have different mesophase–isotropic phase transition temperatures ($T = 72^\circ$C for ZLI-1695 and $T = 95^\circ$C for ZhK-805). These temperatures were scarcely affected by the dopants at equal concentrations (10 wt %) except for with vitamin D_2, which caused minor phase depression (2°C for both matrices). This indicates that the solutes are incorporated into the LC matrices with the least disturbance without strong electrostatic interactions, and the solute size and shape match closely those of the host molecule [8].

It was found that solubility of the compounds with a 'rigid' steroid skeleton was limited to 10 wt %, and for vitamin D_2 only it ranged up to 50 wt %. The well-known fingerprint structures characteristic of an induced cholesteric phase [9] were observed by polarizing microscopy when the prepared mixtures were sandwiched between two glass plates. The sign and pitch of the induced cholesteric helix were determined by the standard procedure [3] using wedge-like LC cells with an area

Liquid Crystals Today ISSN 1464-5181 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/14645180210006824

Table 1. Steroid chiral dopants, characteristics of induced cholesteric helices and calculated helical twisting power in the nematic matrices.

Steroid	Chemical structure	Sense and sign of the helix in ZLI-1695 and ZhK-805	Number of Cano lines		HTP/μm^{-1} mol $frac^{-1}$	
			ZLI-1695	ZhK-805	ZLI-1695	ZhK-805
Cholesterol		Left-handed (−)	12	11	−2.9	−2.8
7-Dehydrocholesterol (provitamin D_3)		Right-handed (+)	11	10	+1.9	+1.8
Cholesterol benzoate		Left-handed (−)	13	12	−2.7	−2.5
7-Dehydrocholesterol benzoate		Left-handed (−)	13	12	−2.9	−2.8
Ergosterol (provitamin D_2)		Right-handed (+)	11	10	+1.9	+1.8
$Lumisterol_3$		Left-handed (−)	10	9	−1.8	−1.6
Ergocalciferol (vitamin D_2)		Left-handed (−)	32	28	−5.9	−5.4

of $15 \times 20\,mm^2$ area and a thickness of 60 μm, with the substrates treated to provide planar boundary conditions for homogeneous alignment of the LC molecules. As is known, a chiral nematic (cholesteric) LC, filled into such a cell, forms a texture in which the quasi-nematic layers are twisted, and the disinclination lines (Cano) occurring at equal distances from one another are easily observed with a polarizing microscope.

As is evident from table 1, only minor variations in the number of Cano lines were observed for all dopants

except for vitamin D_2. This demonstrates that, in contrast to the cholesteric phase, the structural modifications only slightly affect the helical twisting power (HTP)[†] of the steroid chiral dopants (except vitamin D_2). Surprisingly, in spite of the more flexible structure of vitamin D_2, its helical twisting power appears to be around three times higher in comparison with those of compounds with a rigid steroid skeleton (table 1).

As for the sign of the helix, it has been found that only provitamins D_2 and D_3 induce right-handed (or positive) helices, and the other five compounds induce left-handed helices in both nematic matrices. This is can be understood by taking into account the conformational arrangement within the steroid nucleus of the molecules. As has been shown [2, 10] the steroid ring system is usually twisted and can adopt the form of a left- or right-handed helix under the influence of intramolecular methyl–hydrogen interactions and the solvent polarity (which, with few exceptions, correlates with the sign of the Cotton effect [2]).

Hence, on the basis of the example of the two antiisomers lumisterol and ergosterol that induce cholesteric helices of opposite sign, we propose a correspondence between the handedness of the steroid molecular helix and the sign of the induced cholesteric helix in a nematic material. In such a case, the molecular helicity of cholesterol and 7-DHC in the nematic matrix should be of opposite sign since they induce macrohelices of opposite sign (in spite of the fact that the cholesteric phases of both pure compounds exhibit right-handed helices [4]).

To check this assumption we turned our attention to the dynamics of the cholesteric phase induction. Because of the helicity of the steroid moiety, a single molecule may be thought of as a screw and its diffusion under dissolution into a nematic matrix could be seen as analogous to inserting a corkscrew into a cork. Obviously in this case the forward movement of the helical solute should be accompanied by its rotation. Owing to the 'friction' between the steroid molecule and the nematic microenvironment the steroid molecular 'external screw' should involve rotation of the tight-fitting host nematic layers ('internal screw'). We expected that under favourable conditions these microscopic collective rotations might be visualized.

With this aim we observed with a polarizing microscope the dissolving process of a single rod-like steroid crystal placed at the surface of the nematic droplet (ZLI-1695). Using a capillary tube, a nematic droplet of

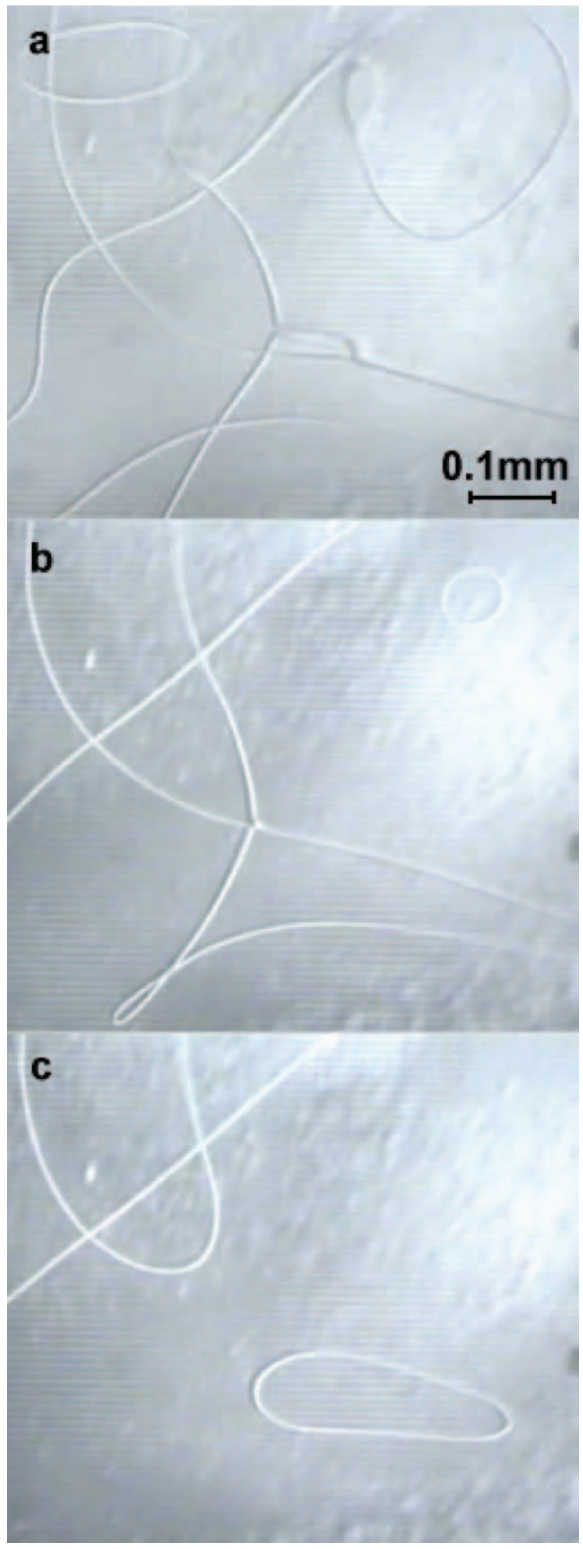


Figure 1. Sequential images of the ZLI-1695 nematic droplet (area $0.67 \times 0.6\,mm^2$) as it spreads over the substrate, taken with a CCD camera attached to a polarizing microscope. The time intervals are 35 s between a) and b) and 50 s between b) and c). The movie is available at ftp://ftp.iop.kiev.ua/pub/effects/movie1.zip

[†]At the dopant concentrations $C < 10\%$ (by mass fraction) the pitch is inversely proportional to C, and the constant of proportionality is called the helical twisting power (HTP) of the chiral dopant. The HTP is defined as $HTP = (P \cdot C)^{-1}$.

diameter 1.5 mm was deposited on the glass substrate without any preliminary treatment. After deposition the drop spread over the plate forming a unit 6 mm in diameter and 1 mm in height. Interestingly, the spreading process was accompanied by slow movement of typical disinclination lines and walls [11] and by the collapsing of closed circles (figure 1).

The drop was bright when viewed by transmitted light between crossed polarizers, suggesting a multidomain structure with domains randomly oriented with respect to one another. However, a well-defined dependence of the light transmission on the plate orientation (twist-angle between crossed polarizers) suggested that the predominant orientation of the director was planar.

Next, an individual rod-like (needle-shaped or prismoidal) steroid crystal of length 0.1×1 mm was deposited on the nematic droplet (ZLI-1695) and the dissolving dynamics was tracked with a polarizing microscope. By following the dissolution course we discovered that for all the compounds crystal dissolution was accompanied by mechanical rotation (see figure 2).

Certain common features emerged on closer examination of the process, and are summarised as follows.

1. For all steroid compounds the rotation direction correlated with the sign of the induced cholesteric helix. A clockwise rotation was inherent to the compounds that induced the right-handed helices in the LC cell and *vice versa*; that is, the clockwise rotation was observed only for the crystals of provitamins D_2 and D_3, and for the other steroids the rotation occurred in an anticlockwise direction. Worthy of mention are the opposite rotation directions of cholesterol and 7-DHC, which confirm the validity of our suggestion about the opposite helicity of these two compounds in the nematic LC matrix resulting in induced macrohelices of opposite sign.
2. The rotation speed of a crystal depended on its dissolution rate and, to a lesser degree, on the crystal size; that is, more massive crystals rotated more slowly. A uniform rotation with a speed of $6^\circ\,s^{-1}$ was recorded in the case of a needle-shaped 7-DHC crystal of 0.1 mm length (figure 2). Dissolution of the vitamin D_2 crystal was noted to occur much more efficiently as compared with that for all the other compounds, and, as a result, the vitamin D_2 crystal of 1 mm length exhibited the lowest speed of rotation: $\sim 0.5^\circ\,s^{-1}$ (see figure 3).
3. At room temperature, rotation was observed only in the case of the ZLI-1695 droplets and no rotation took place in the case of the more viscous ZhK-805; it was necessary to heat the substrate to 60°C to initiate the rotation in this case. It must be emphasized that rotation was observed neither in a viscous solvent (glycerin), nor in the isotropic phase upon heating of both LCs. Hence, we may conclude that long-range ordering in the nematic crystal is responsible for the effect revealed.

The above results demonstrate how the helicity of a chiral dopant is related to the induced macrohelix, and, in principle, the rotary motion can be used as a simple method to determine the sign of an induced cholesteric helix in a nematic LC.

We suggest that the effect revealed demonstrates the real-time transmission of chiral information. It has much in common with known rotary motions caused by thermomechanical interactions in cholesteric crystals

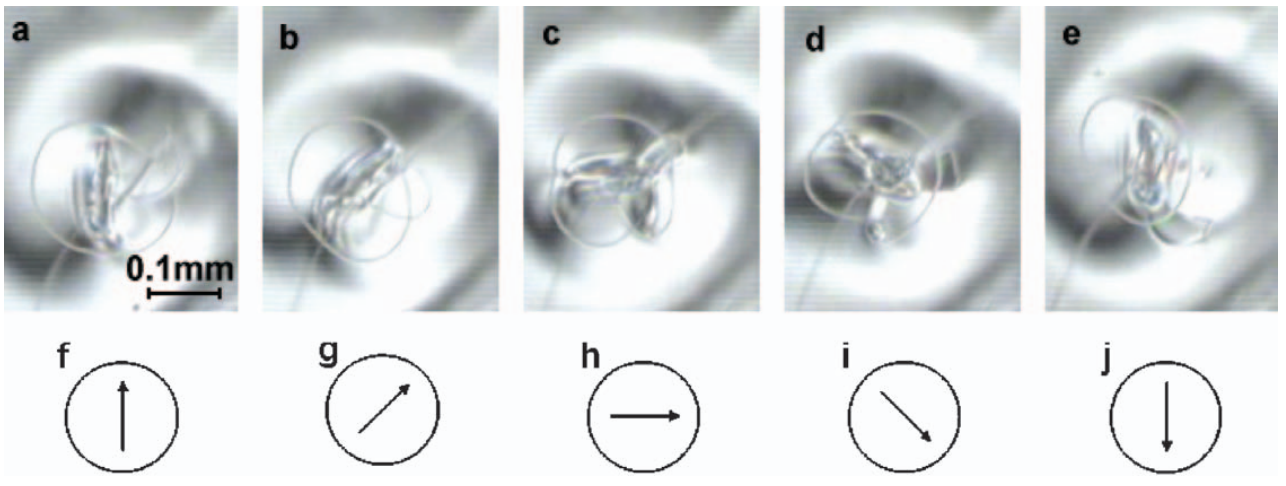


Figure 2. Sequential images (a–e) of the clockwise rotation of the 7-DHC crystal at the surface of the ZLI-1695 nematic droplet, taken at time intervals of 7.5 s; and schematic representations (f–j) of the corresponding crystal positions. The movie is available at ftp://ftp.iop.kiev.ua/pub/effects/movie2.zip

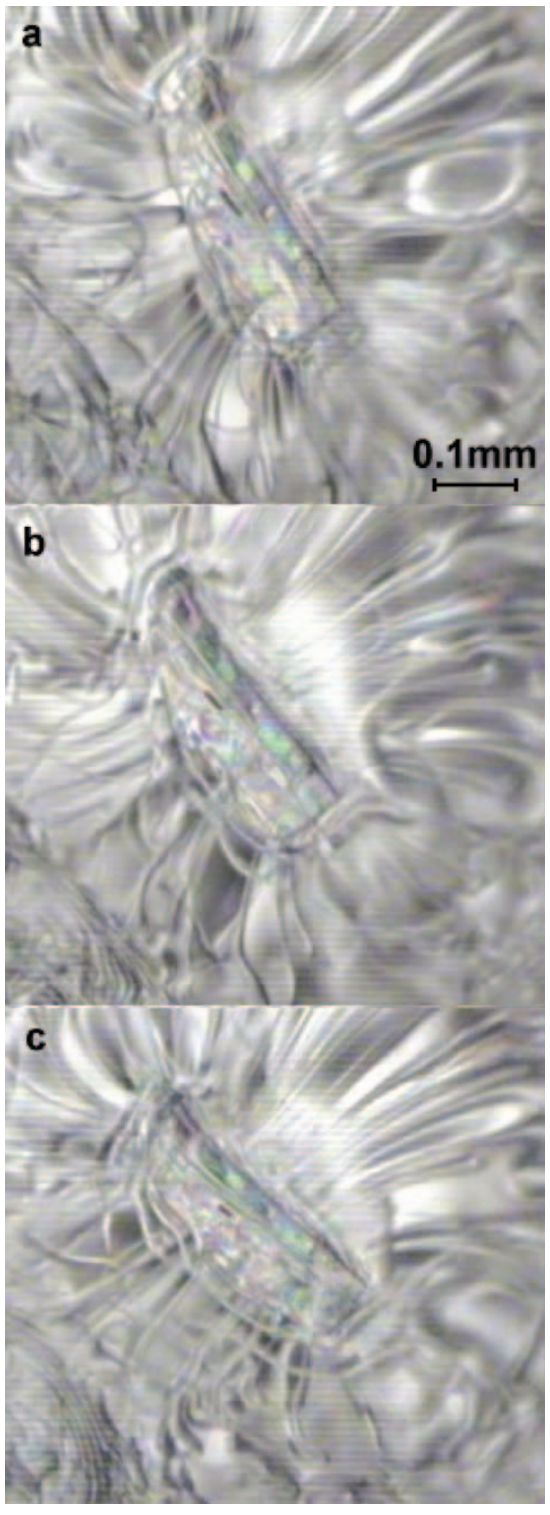


Figure 3. Sequential images (a–c) of the anticlockwise rotation of the vitamin D_2 crystal at the ZLI-1695 nematic droplet, taken with time intervals of 15 s. The movie is available at ftp://ftp.iop.kiev.ua/pub/effects/movie3.zip

(Lehmann's effect [9]), but in our case the role of temperature gradient is played by the gradient of solute concentration.

Obviously, being bound to the drop's surface by cohesion, the rod-like steroid crystal rotates together with the upper layer of the nematic droplet, thus demonstrating visually the induction of the cholesteric helix. To the best of our knowledge, this is the first observation of a monodirectional rotation driven by direct transformation of chemical dissolution energy into mechanical rotational energy. We think the origin of the effect revealed is attributable to the low twisting energy in the nematic matrix that is only the least part ($\sim 10^{-5}$) of the total energy related to the parallel packing in the layer [9]. Twisting of the layers would thus be expected in the case where the macrohelix is stretched or contracted. In Lehmann's effect the specific thermomechanical interactions responsible for the rotary motion were initiated by the temperature gradient that caused a one-sided helix stretch under thermal expansion [9]. In our case the pitch variability in the induced helix is conditioned by the chemical potential gradient arising from solute diffusion. We were fortunate that for ZLI-1695 the dissolution rate of the steroid crystal and the elastic energies in the nematic droplet were properly related at room temperature.

We thank G. Chilaya for help with ZhK-805; R. Weiss for advice and W. Becker (Merck) for help with ZLI-1695; Yu. Reznikov and V. Reshetnyak for useful discussions and D. Fedorenko for technical assistance.

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