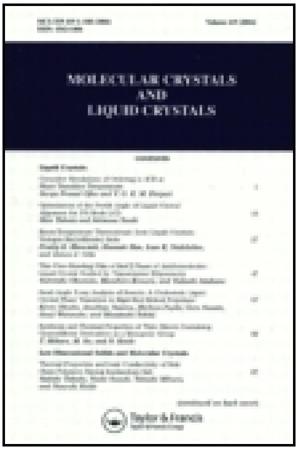

Molecular Crystals and Liquid Crystals

Rotation of Single Crystals of Chiral Dopants at The Top of a Nematic Droplet: Factors Affecting the Angular Velocity

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Version of record first published: 22 Sep 2010

To cite this article: Igor Gvozdovskyy & Longin Lisetski (2007): Rotation of Single Crystals of Chiral Dopants at The Top of a Nematic Droplet: Factors Affecting the Angular Velocity, Molecular Crystals and Liquid Crystals, 475:1, 113-122

To link to this article: http://dx.doi.org/10.1080/15421400701681331

Mol. Cryst. Liq. Cryst., Vol. 475, pp. 113–122, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701681331

Rotation of Single Crystals of Chiral Dopants at The Top of a Nematic Droplet: Factors Affecting the Angular Velocity

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In the Lehmann-type effect of rotation of small single crystals of chiral substances during their dissolutionat the top of a nematic droplet the angular velocity of rotation of the chiral dopant crystals is experimentally shown to be dependent on the crystal dimensions, helical twisting power of the dopant (determined in independent measurements) and viscosity of the nematic solvent, whereas no rotation was observed for non-chiral dopants or in isotropic solvents under the same conditions. For systematic series of dopants (e.g., cholesterol esters), linear dependencies between the angular velocity and helical twisting power were found. It is argued that the obtained results (a) suggest a novel method for evaluation of helical twisting power, especially useful for dopants of weak chirality, and (b) are a direct evidence of transformation of the energy of chiral interactions into the energy of molecular movement.

Keywords: chiral and non-chiral dopants; cholesteric mesophase; Lehmann-type effect; liquid crystal droplets

INTRODUCTION

Dissolution of small amounts of chiral dopants in nematic liquid crystals (NLC) is known to result in formation of the cholesteric mesophase, characterized by the preferred orientation of the long axes

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The authors thank W. Becker (Merck) for generous gift with the chiral dopants (ZLI-3786 and ZLI-0811) and nematic liquid crystal K15 (5CB) and Dr. N. Novikova (A. V. Bogatsky Physico-Chemical Institute, NAS of Ukraine) for providing us with some cholesterol esters.

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of anisometric molecules director ***n***, rotating along the helix axis. The twisting sense of the cholesteric helix can be right- or left-handed, depending upon the nature of chiral dopants and the molecular interaction between chiral dopants and NLC solvent molecules. For the cholesteric phase induced by a chiral compound with concentration c, the wavenumber is written as: $q_0 = 4\pi\beta{\cdot}c$, where β is the helical twisting power (HTP) of the dopant [1–5]. In this paper, main attention is paid to the determination of the twisting sense and HTP of cholesteric helix induced in nematics by various chiral dopants.

It is known that the helical structure of cholesteric liquid crystals (ChLCs) can give rise to various dynamical effects. The first dynamical experiment reported in liquid crystal physics was the Lehmann rotation, when the temperature gradient parallel to the cholesteric helix axis caused uniform rotation of the director structure in a cholesteric liquid-crystalline droplet [6].

Later, it was shown that the rotation effect could be obtained using a static electric field instead of the temperature gradient, with an external electric field applied to a cholesteric droplet [7], resulting in the so-called "electromechanical effect" of Lehmann's rotation.

Recently, a coherent precession of chiral molecules forming a Langmuir monolayer spread on glycerol surface has been reported [8]. The coherent rotational motion of chiral molecules in the monolayer was attributed to the difference in the chemical potential of water molecules transferred across the air-liquid interface. In the author 's opinion, the rotation effect of chiral molecules that formed two-dimensional liquid crystals can be regarded as a monomolecular-layer analogue of Lehmann's effect.

A few years ago, we observed, on the real time scale, the rotational motion of a small steroid single crystal on a nematic droplet during its dissolution and accompanying induction of the cholesteric phase [9,10]. The discovered effect was considered as an analogue of the Lehmann rotation, with an evidence of the concentration gradient of chiral molecules along the full thickness of a nematic droplet.

In this work, our studies of the effect of rotation of single crystal of chiral dopants at the top of a nematic droplet [9,10] were extended to include chiral substances of different chemical nature and different HTP values (including non-chiral substances), as well as nematic solvents with different macroscopic properties.

MATERIALS AND METHODS

To prove that the rotation effect observed in [9,10] is a general feature for all chiral dopants, we used various kinds of chiral dopants with steroid and non-steroid molecular structures. As steroid chiral dopants, we used cholesterol derivatives. Non-steroid chiral substances were represented by two pairs of enantiomers–ZLI-4571 (S-1011), ZLI-4572 (R-1011) and ZLI-0811 (S-811), ZLI-3786 (R-811) presented by Merck, 1-S-(–)-camphor and L-menthol presented by Enamine Ltd. and chromeno-[2,3-*q*]-acridines (CA).

Non-chiral dopants used for reference experiments carried out under the same conditions included benzophenone, imidazole and (±)-camphor from Enamine Ltd. and methyl red (MR), as well as non-chiral solid single crystals grown from (1:1) equimolar mixture of R-811 and S-811.

All chiral and non-chiral dopants were recrystallized under appropriately chosen crystallization conditions to form rod-like (prismoidal) crystals of similar shape, which should have made the observation of rotation effect easier and correct, but only for two pairs of enantiomers obtained from Merck the rod-like crystals were of needle-shaped. The overall dimensions of the crystals were $0.1\div1.2\,\mathrm{mm}$ (length) and $0.05\div0.3\,\mathrm{mm}$ (width). The maximum of the size distribution of prismoidal crystals of cholesterol derivatives after recrystallization closely corresponds to the crystals with overall dimensions $0.2\times0.1\,\mathrm{mm}^2$.

The single crystal samples were dissolved in nematics 4-methoxybenzylidene-4′-butylaniline (MBBA) and 4-*n*-pentyl-4′-cyanobiphenyl (5CB) (Merck, Germany), which had differed rotational viscosity γ_1 values, namely $\gamma_1 = 109.3\,\mathrm{mPa{\cdot}s}$ at 25°C for MBBA and $\gamma_1 = 77.7\,\mathrm{mPa\cdot s}$ at 26°C for 5CB [11,12]. The choice of these nematics was also suggested by their extensively reported use for induction of helical twisting [1,2,4].

To determine of the helical twisting power (HTP) value of chiral dopands we used the well-known Cano-Grandjean method. To determine the sense of the cholesteric helix induced by chiral dopands in nematics was applied the Cano-Grandjean method based on the colour shift of stripes in a wedge-like LC cell [13]. The twisting sense of the cholesteric helix is easily determined, namely, if the colour stripes are shifted towards the origin of the wedge upon clockwise rotation of the polarizer, then the cholesteric helix is right-handed (or plus "+") and vice versa (see http://www.iop.kiev.ua/~gvozdovskyy/Schedule_Movies.htm [download movie6]).

The dissolution process of single crystals of chiral and non-chiral dopants on the nematic droplets was studied at the room temperature by using a simple experimental set-up shown in Figure 1. The nematic droplet was deposited onto the glass substrate by the tube capillary. After deposition the droplet was forming a segment with overall dimensions $5\div6\,\mathrm{mm}$ diameter and $1\div1.5\,\mathrm{mm}$ height. At the top of a

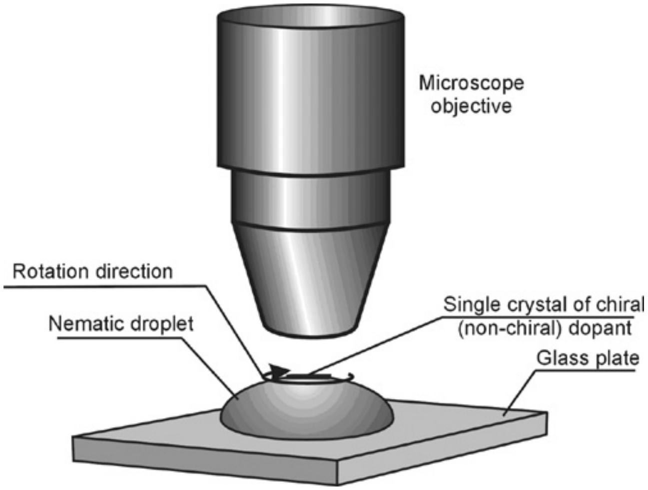


FIGURE 1 Experimental set-up for observation of the dissolution of a single crystal.

nematic droplet we observed in microscope the disclination walls, which disappeared in a short time (about 3–5 min) (see http://www.iop.kiev.ua/~gvozdovskyy/Schedule_Movies.htm [download movie1]). After this procedure the single crystal was placed at the top of the nematic droplet. The dissolution of the crystal was observed by visual method through the polarizing microscope or recorded using a CCD camera. In order to determine the angular velocity of rotation of the single crystal, an eyepiece with angular scale and a stopwatch were used.

RESULTS AND DISCUSSION

The twisting sense of the induced cholesteric helix and HTP values of chiral dopants are shown in Table 1.

For all chiral dopants, the rotational motion of crystals was similar to the previously reported picture [10]. The dissolution of crystals of the chiral dopants with steroid molecular structures was accompanied by the counterclockwise rotation. The correlation between the direction of rotation and helix sense of the induced cholesteric phase was observed. In the case of non-steroid chiral dopants, the opposite directions of rotation of the dissolving crystals were also obtained. So, for the enantiomer pair S-811 and R-811 (or S-1011 and R-1011) the counterclockwise and clockwise rotations were observed, respectively (see for example http://www.iop.kiev.ua/~gvozdovskyy/Schedule_Movies.htm [download movie2], [download movie3]). In this respect

TABLE 1 Angular Velocity and Direction of Rotation of Small Crystals of Chiral Dopants under their Dissolution at the Top of a Nematic Droplet (MBBA, 5CB), Helical Twisting Power and Sense of the Cholesteric Helix Induced by the Chiral Dopants

	HTP (μm wt.-%)$^{-1}$		Angular velocity ω, °/s		Rotation direction
Chiral dopants	MBBA	5CB	MBBA	5CB	MBBA, 5CB
Cholesterol	−0.0073	−0.0170	4.09	2.1	Counterclockwise
Cholesterol chloride	−0.0301	−0.0181	11.17	1.75	Counterclockwise
Cholesterol iodide	−0.0364	−0.0168	14.5	1.7	Counterclockwise
Cholesterol acetate	−0.0351	−0.0314	13.35	4.24	Counterclockwise
Thiocholesterol propionate	−0.0309	−0.0431	12.57	5.36	Counterclockwise
Cholesterol butyrate	−0.0409	−0.0276	16.63	4.07	Counterclockwise
Cholesterol valerate	−0.0295	−0.0342	12.36	5.01	Counterclockwise
Cholesterol caproate	−0.0406	−0.0248	16.36	2.91	Counterclockwise
Cholesterol enantate	−0.0394	−0.0255	15.65	3.26	Counterclockwise
Cholesterol pelargonate	−0.0377	−0.0220	15.18	2.21	Counterclockwise
S-811 (ZLI-811)	Not measured	−0.077	Not measured	4.45	Counterclockwise
R-811 (ZLI-3786)	Not measured	+0.0782	Not measured	3.68	clockwise
S-1011 (ZLI-4571)	Not measured	−0.1209	Not measured	14.15	Counterclockwise
R-1011 (ZLI-4572)	Not measured	+0.1215	Not measured	15.76	clockwise
1-S-(−)-camphor	Not measured	−0.0032	Not measured	1.32	Counterclockwise
L-menthol	−0.0093	−0.0074	3.85	1.54	Counterclockwise
Chromeno-[2,3-*q*]-acridines	−0.001	Not measured	0.011	Not measured	Counterclockwise

the observed correlation between the rotation directions of crystals and twisting sense of the cholesteric helix induced by these enantiomers is a behavior very similar to the molecular precession observed by Tabe and Yokoyama for Langmuir monolayers from chiral dopants (R)-OPOB and (S)-OPOB [8]. Madhusudana and Pratibha [7] have also observed a reversal of the rotational motion for the opposite hand of the helix for Lehmann effect in an external electric field for cholesteric droplets surrounded by the isotropic medium in a biphasic region near the cholesteric-isotropic phase transition.

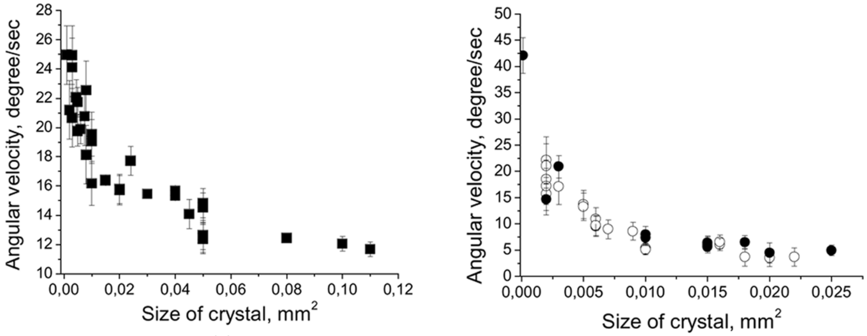
It may be assumed that if the effect of rotation is related to chirality of the dopant molecules, then no rotation of single crystals of non-chiral compounds will be observed. To verify this, we dissolved various non-chiral dopants at the top of nematic droplets under the same conditions. It is known that single crystal formed from a (1:1) equimolar mixture of two enantiomers R-811 and S-811, as well as single crystals of (±)-camphor containing an (1:1) equimolar mixture of 1-R-(+)- and 1-S-(−)-camphor are non-chiral. In our observations using a polarizing microscope, the dissolution of these "racemic" single crystals, as well as crystals of non-chiral substances (benzophenone, imidazole, and methyl red) was accompanied by no rotational motion (see for example http://www.iop.kiev.ua/~gvozdovskyy/Schedule_Movies.htm [download movie4], [download movie5]), which fully confirmed our assumption. From this experiment we can conclude that chirality is a principal cause of the rotation effect, observed for crystals of both steroid and non-steroid molecular structures.

Our observations with non-chiral dopants are very similar to those of Tabe and Yokoyama [7], who found that all chiral compounds forming Langmuir monolayers spread on glycerol surface in their experiments exhibited similar spatio-temporal patterns, whereas for non-chiral monolayer such patterns were not observed.

The emerging picture shows the small single crystals rotating together with quasinematic layers, and the direction of rotation is determined by the sign of helical twisting power (HTP, β) of the chiral dopant.

The angular velocity of single crystals dissolved at the top of the nematic droplet (MBBA) as function of crystals size is shown in Figure 2. Data shown in Figure 2(a) refer to different independent measurements for prismoidal crystals of cholesteryl valerate.

It is important to note that dissolution of single crystals of enantiomers R-811 and S-811 (or R-1011 and R-1011) with the same mass (or size) at the top of a nematic droplet (MBBA) is accompanied by rotation with the same angular velocity as shown in Figure 2(b), but in opposite directions (see Table 1).



(a) (b)

FIGURE 2 The angular velocity of single crystals dissolved at the top of the nematic droplet (MBBA) as function of crystals size for: a) prismoidal crystals of cholesterol valerate; b) needle-shaped crystals of the two enantiomers: S-811(open circles) and R-811 (solid circles).

In this work, we have experimentally confirmed that the angular velocity is dependent on the twisting power of chiral dopant, i.e., the rotation motion of crystals is faster when of the chiral dopants with higher β.

Experimentally it is obtained that the angular velocity is proportional to the helical twisting power of the dopant, as shown in Figure 3 for cholesterol esters crystals with average size 0.02 mm^2.

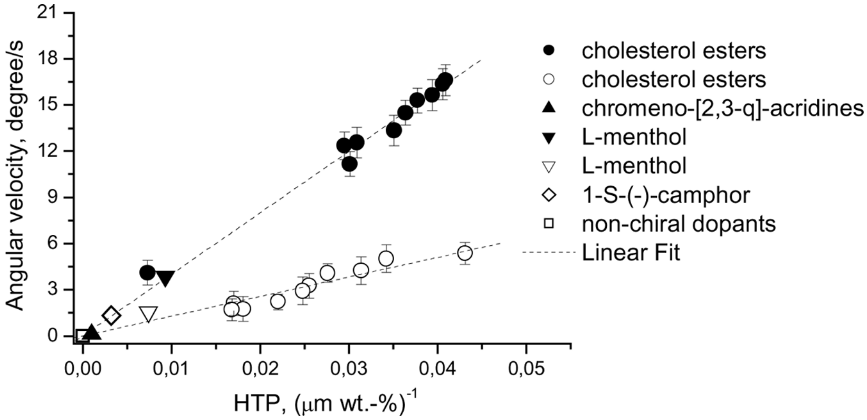


FIGURE 3 The angular velocity of single crystals of various chiral dopants dissolved at the top of a nematic droplet as function of HTP values of these substances: MBBA (solid symbols) and 5CB (open symbols).

For the nematics used (MBBA and 5CB), the observed rotation velocity ω is directly proportional to the HTP value of the chiral dopant as shown in Figure 3. For the case of the Lehmann effect for Langmuir monolayer, Tabe and Yokoyama experimentally found that the speed of molecular precession was also proportional to the chiral strength and concentration gradient [8].

This dependence holds, with rather good accuracy, for a large number of chiral dopants (see Fig. 2). In our opinion, the described procedure may be used as a method for determination of HTP (value and twisting sense) of an unknown chiral substance. The information on HTP will be more accurate and more readily obtained as compared, say, to the Cano-wedge method. In some cases (when the HTP value is small and/or the available amount of the tested substance is limited), the proposed method would be the only way to estimate the HTP magnitude and the helix sense. For example, due to a very low solubility of the chromeno-[2,3-*q*]-acridines (CA) in MBBA, we applied this procedure for determination of value and twisting sense using the linear plot of the angular velocity ω vs. HTP in MBBA (see Fig. 3). in our experiments with CA we observed rotation with a small angular velocity (about 0.001 degree/s) and the counterclockwise direction, suggesting the left-handed helical twisting.

Slopes of the linear plots (ω vs. HTP) are clearly correlated with the rotational viscosity γ_1 of the nematic solvent. From Figure 2, we can conclude that higher viscosity γ_1 does not slow down the movement of the dissolved particle, but leads to its faster rotation. The apparent contradiction, however, is fully consistent with the picture based on the analogy with Reynolds number in hydrodynamics [14], which can be written as:

$$v = \mathrm{Re} \cdot \mu \cdot \frac{1}{\rho \cdot d},$$

where v is the flow velocity, d – tube diameter, ρ – liquid density, μ – dynamical viscosity of the liquid and Re is the Reynolds number. Making straightforward substitutions $v \rightarrow \omega$, $d \rightarrow l$ (where l is a characteristic dimension of the crystal surface contacting the nematic droplet), we come to an expression:

$$\omega = \beta \cdot \gamma_1 \cdot \frac{1}{\rho \cdot l},$$

where γ_1 and ρ are the rotational viscosity and density of a nematic liquid crystal, respectively, and β is the measure of helical twisting power. Thus, we can conclude that $\omega \sim \gamma_1$, which ensures correct unit dimensions.

CONCLUSIONS

Principal features of the results obtained by including those that we observed in this work can be summarized as follows. The dissolution of small single crystals of chiral dopants with various molecular structure placed at the top of a nematic droplet was shown to be accompanied by the crystal rotation. For all chiral compounds used, the correlation between the rotation direction and the twisting sense of induced cholesteric helix was observed. It has been found that the angular velocity of the crystal rotation is dependent on the HTP value of the chiral dopants and the crystal size. The rotation was not observed in isotropic viscous solvents or in the isotropic phase obtained upon heating of the nematic solvent, suggesting that the long range ordering in the nematic liquid crystals is responsible for the observed effect of rotation. Also, the effect of the crystal rotation has been observed only for chiral dopants, as distinct from crystals of non-chiral substances studied under the same conditions. The obtained dependencies of the rotation velocity on the helical twisting power of the dopant and the rotational viscosity of the nematic solvent are explained within a simple theoretical model using an analogy with the Reynolds number of conventional hydrodynamics. The observed rotation effect can be a base for a novel method of evaluation of helical twisting power, which can be especially useful for dopants of weak chirality, being much more sensitive than the Cano-wedge method. Our other claim is that the rotation effect studied is, in fact, a direct observation of transformation of the energy of chiral interactions into the energy of molecular movement, which is closely related to the problem of molecular motors.

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