

Rotation of single crystals of chiral dopants at the top of a nematic droplet: Analogy with Lehmann effect

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Abstract. Detailed studies are reported of the Lehmann-type effect of rotation of small single crystals of chiral substances during their dissolution at the top of a nematic droplet, which was first noted in our previous works. The rotation effect is shown to be essentially dependent on the dopant chirality. The angular velocity of the 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), the angular velocity was proportional to the helical-twisting power; with different nematic matrices, the observed angular velocity was proportional to the rotational-viscosity coefficient γ_1 ; also, in a certain size range, it was inversely proportional to the characteristic linear dimension of the dissolved crystal. Basing on unit dimensions arguments, a semi-empirical equation is proposed giving a common quantitative description of the whole set of experimental data obtained. It is argued that the obtained results a) suggest a novel method for the evaluation of the helical-twisting power, especially useful for dopants of weak chirality, and b) that they are a direct evidence of transformation of the energy of chiral interactions into the energy of the molecular movement.

PACS. 64.70.Md Transitions in liquid crystals – 61.30.Eb Experimental determinations of smectic, nematic, cholesteric, and other structures – 47.55.Kf Multiphase and stratified flows: Particle-laden flows

1 Introduction

Dissolution of small amounts of chiral dopants in nematic liquid crystals (NLC) is known to result in the formation of the cholesteric mesophase, characterized by the preferred orientation of the long axes of the anisometric molecules director $\mathbf{n}$, 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 wave number is written as $q_0 = 4\pi \cdot \beta \cdot c$, where the efficiency of the dopant to induce a cholesteric phase with helical pitch $P = 2\pi/q_0$ in a liquid-crystalline matrix is expressed by its helical-twisting power (HTP, β). This parameter reflects the amount of dopant needed to reach a cholesteric phase with a certain pitch P . The pitch then is inversely

proportional to the concentration c and HTP of dopant: $P = 1/2 \cdot (\beta \cdot c)^{-1}$ [1–5]. In this paper, the main attention is paid to the determination of the twisting sense and HTP of the 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 a uniform rotation of the director structure in a cholesteric liquid-crystalline droplet [6] and a theoretical treatment of the effect has been given by other authors [7–10]. 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 [11], resulting in the so-called “electromechanical effect” of Lehmann’s rotation, which was theoretically interpreted [8, 9, 12, 13]. Recently, a coherent precession of chiral molecules forming a Langmuir monolayer spread on glycerol surface has been reported [14]. The coherent rotational motion of chiral

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molecules in the monolayer was attributed to the difference in the chemical potential of water molecules transferred across the air-liquid interface [14–16]. 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 [14]. 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 [17,18]. 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 [17,18] 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.

2 Materials and methods

To prove that the rotation effect observed in [17,18] 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. Two pairs of enantiomers ZLI-4571 (S-1011), ZLI-4572 (R-1011) and ZLI-0811 (S-811), ZLI-3786 (R-811), obtained by Merck, represented non-steroid chiral substances.

Non-chiral dopants used for reference experiments carried out under the same conditions included benzophenone, imidazole and ($\pm$)-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. The overall dimensions of the crystals were 0.1–1.2 mm (length) and 0.05–0.3 mm (width). The single-crystal samples were dissolved in several different nematics, including: (1 : 1) mixture of 4-*n*-butyl- and 4-*n*-hexyl-*trans*-cyclohexancarboxylic acids (CHCA, ZhK-805); 4-methoxybenzylidene-4'-butylaniline (MBBA); 4-*n*-pentyl-4'-cyanobiphenyl (5CB); a multicomponent mixture with 5CB as the main component (E7); a nematic mixture MLC-6882 (Merck, Germany). These nematics had different values of rotational-viscosity γ_1 values, namely $\gamma_1 = 185 \text{ mPa} \cdot \text{s}$ at 25°C for CHCA [19], $\gamma_1 = 153 \text{ mPa} \cdot \text{s}$ at 20°C for MBBA [20–22], $\gamma_1 = 135 \text{ mPa} \cdot \text{s}$ at 26°C for E7 [21,22], $\gamma_1 = 108 \text{ mPa} \cdot \text{s}$ at 20°C for MLC-6882 [23] and $\gamma_1 = 68.2 \text{ mPa} \cdot \text{s}$ at 20°C [23] (according to data given in [21,24–26], this value corresponds to $\sim 28^\circ\text{C}$) for 5CB. The choice of these nematics was also suggested by their extensively reported use for induction of helical twisting [1,2,4]. To determine the sense of the cholesteric helix induced by chiral dopants in nematics we applied the Grandjean-Cano method based on the colour shift in

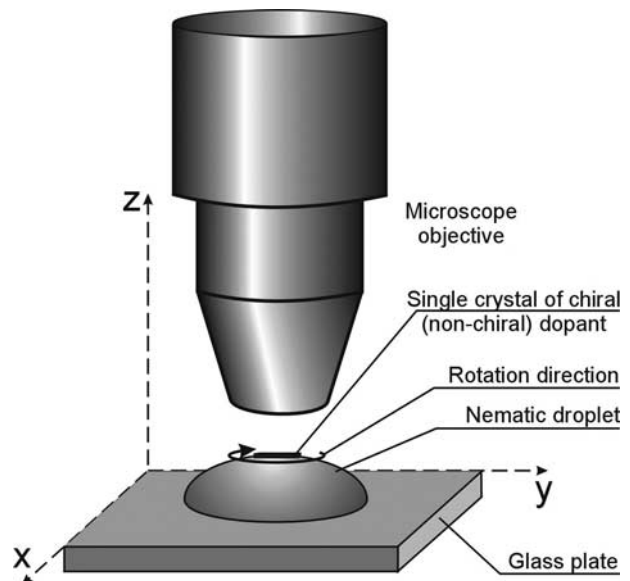


Fig. 1. Experimental set-up for observation of the dissolution of a single crystal.

a wedge-like LC cell [27]. In the wedge-like cell, alongside with Cano disclinations, the interference fringes could also be observed under a polarizing microscope with crossed polarizers. For a right-handed cholesteric ($q_0 > 0$), the interference fringes are shifted towards regions of smaller wedge thickness when the polarizer (analyzer) rotates in the clockwise (or counterclockwise, depending upon observation conditions) direction. For a left-handed cholesteric ($q_0 < 0$), the movement in the opposite direction is observed (see http://www.iop.kiev.ua/~gvozdevsky/Schedule_Movies.htm (download movie6)).

The dissolution process of single crystals of chiral and non-chiral dopants on the nematic droplets was studied at room temperature by using a simple experimental set-up shown in Figure 1.

The nematic droplet was deposited onto the glass substrate by a tube capillary. After deposition the droplet was forming a segment with overall dimensions 5–6 mm diameter and 1–1.5 mm height. At the top of the nematic droplet we observed (under a microscope) the disclination walls, which disappeared in a short time (about 3–5 min) (see http://www.iop.kiev.ua/~gvozdevsky/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 visually 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.

3 Results and discussion

For all chiral dopants, the rotational motion of crystals was similar to the previously reported picture [18]. 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, different directions of rotation of the dissolving crystals were observed. Thus, for the enantiomer pair S-811 and R-811 (or S-1011 and R-1011) the counterclockwise and clockwise rotations were observed, respectively (see, *e.g.*, http://www.iop.kiev.ua/~gvozдовskyy/Schedule_Movies.htm (download movie2), (download movie3)). In this respect the observed correlation between the rotation direction of the dissolved crystals and the 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 formed by chiral dopants (R)-OPOB and (S)-OPOB [14]. Madhusudana and Pratibha [11] have also observed a reversal of the rotational motion for the opposite helix handedness in their experiments on the 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.

One can assume that if the effect of rotation is related to the chirality of the dopant molecules, 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. In our observations using a polarizing microscope, we have never noted any signs of rotational motion (see http://www.iop.kiev.ua/~gvozдовskyy/Schedule_Movies.htm (download movie4), (download movie5)).

Our observations with non-chiral dopants are very similar to those of Tabe and Yokoyama [14], 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. Basing on our experimental results [17], a simple model of the rotation effect of steroid crystals was proposed [18], showing that the direction of rotation under polarizing microscope should be determined by the sign of helical-twisting power (HTP, β) of the chiral dopant.

In this work, we have experimentally confirmed that the angular velocity is dependent on the twisting power of the chiral dopant, *i.e.*, the rotation motion of crystals is faster for chiral dopants with higher β . It is important to note that the 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 is accompanied by rotation with the same angular velocity, but in opposite directions. In addition, the angular velocity was found to be proportional to the helical-twisting power of the dopant, as shown in Figure 2 for cholesterol esters crystals with the same average size (0.2 mm in length and 0.1 mm in width).

As was mentioned in [18], the angular velocity of a small single crystal is dependent on the crystal size. For

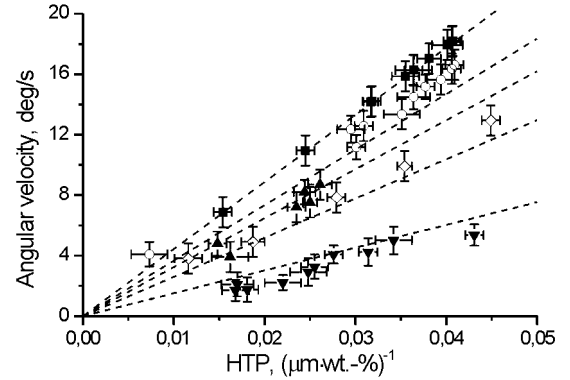


Fig. 2. The angular velocity of steroid single crystals dissolved at the top of nematic droplets of different nematics as a function of HTP values of dissolved chiral substances. Experimental data: CHCA (solid squares), MBBA (open circles), E7 (solid up triangles), MLC-6882 (open diamonds) and 5CB (solid down triangles). Dashed lines were calculated using equation (1).

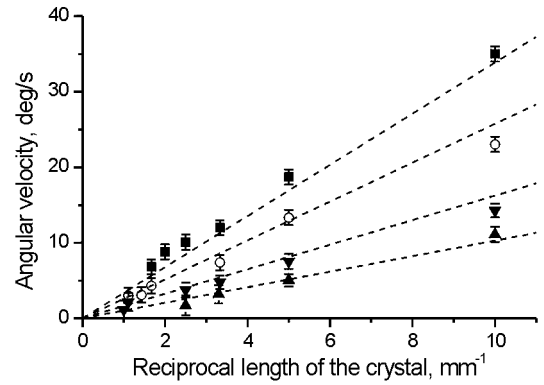


Fig. 3. The angular velocity of cholesterol acetate single crystals dissolved at the top of nematic droplets of different nematics as a function of the reciprocal length of the crystal. Experimental data: CHCA (solid squares), MBBA (open circles), E7 (solid up triangles) and 5CB (solid down triangles). Dashed lines were calculated using equation (1).

all chiral dopants we have experimentally found that for single crystals of a similar shape dissolved at the top of a nematic droplet the angular velocity is inversely proportional to the crystal length. This is demonstrated in Figure 3 for cholesterol acetate crystals dissolved in different nematics (CHCA, MBBA, E7 and 5CB).

For the nematics used, the observed rotation velocity ω is directly proportional to the HTP value of the chiral dopant. The same result ($\omega \sim \beta$) follows from the rotation model proposed in [18].

One could note that, in the case of the Lehmann effect for Langmuir monolayers, Tabe and Yokoyama experimentally found that the speed of molecular precession was also proportional to the chiral strength and concentration gradient [14–16].

This dependence holds, with rather good accuracy, for a large number of steroid chiral dopants (see Fig. 2). In our opinion, the described procedure may be used as a

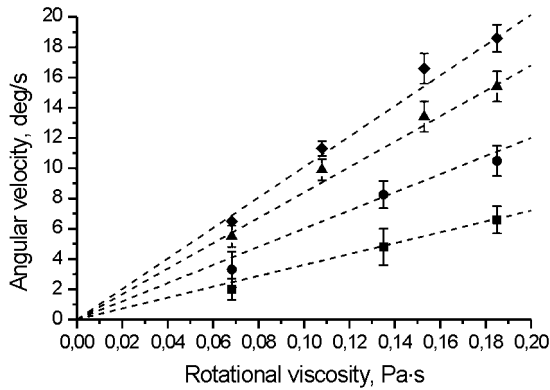


Fig. 4. The angular velocity of a single crystal dissolved at the top of a nematic droplet as a function of rotational viscosity for fixed chiral strength. Experimental data: HTP ≈ 0.015 (solid squares), HTP ≈ 0.025 (solid circles), HTP ≈ 0.035 (solid triangles) and HTP ≈ 0.042 (solid diamonds). Dashed lines were calculated using equation (1).

method for the 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 very 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.

Slopes of the linear plots (ω vs. HTP) are clearly correlated with the rotational viscosity γ_1 of the nematic solvent. From Figure 2 and Figure 4 we can conclude that a higher viscosity 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 following picture. When the crystal is being dissolved, the chiral molecules are incorporated on the molecular level into the orientationally ordered nematic solvent. The dissolved chiral molecules are diffusing both in the horizontal (x, y)-planes and in the z -direction (Fig. 1), forming an induced cholesteric structure in the upper part of the nematic droplet. Since chiral molecules are diffusing downwards in the nematic droplet (in the z -direction) gradually, their distribution is not uniform, and the concentration gradient of the chiral molecules gives rise to the Lehmann-type rotation of the director in quasi-nematic layers (x, y). This process, with appropriate expressions for the rotation velocity of the director, was considered in detail in [7–10, 12, 13, 15, 16]. As a subsequent stage of this process (a new effect not considered in [7–10, 12, 13, 15, 16]), the angular momentum of this rotation is transferred to the crystal piece that has not been yet dissolved; it begins to rotate in the opposite direction to ensure the conservation of the angular momentum. The only feasible mechanism by which this transfer can be realized is via the viscosity of the liquid medium, *i.e.*, of the nematic. The simplest and the most apparent expression for the rotational velocity in these conditions that leads

to correct unit dimensions is

$$\omega = a \cdot \beta \cdot \gamma_1 \cdot \frac{1}{\rho \cdot l}, \quad (1)$$

where a is a dimensionless fitting constant, β and ρ are the helical-twisting power (HTP) and the density of a liquid crystal, respectively. From the set of dynamic viscosity coefficients of nematics as anisotropic liquids (see, *e.g.*, [1]), the rotational viscosity γ_1 is taken as the most appropriate and natural choice for our experimental conditions. One can easily see that equation (1), with $\omega \sim \gamma_1$, ensures correct unit dimensions in the left- and right-hand sides.

The linear character of the plots (ω vs. γ_1) for fixed HTP (Fig. 4), with the extrapolation leading to the origin of the coordinates, is clearly correlated with our conclusion that ω is proportional to γ_1 , equation (1); the experimental data (symbols) and calculated linear plots (dashed lines) are in rather good agreement.

If β is taken in $(\mu\text{m} \cdot \text{wt.}\%)^{-1}$, γ_1 in $(\text{Pa} \cdot \text{s})$, l in (mm) , the fitting constant $a/\rho = 480$ for all the dashed lines in Figures 2–4.

This interpretation of the results obtained is but a first step towards a deeper understanding of the observed phenomenon. A detailed theoretical description should, of course, involve the diffusion coefficients, as well as the dynamics of the solution process. The solution, however, is not straightforward, because the diffusion coefficients are expected to have substantially different values and exhibit essentially different behavior in the directions parallel and perpendicular to the helical axis. The movement of the dissolved particles is, in fact, a complex superposition of translational and rotational components, ensuring conservation of both linear and angular momentum. However, we consider that our simplified description of the rotational motion, supported by a rather large set of experimental data obtained using a number of different substances, can give a certain insight into the nature of chirality and helical twisting in anisotropic organic media.

4 Conclusions

Principal features of the results obtained in this work can be summarized as follows. The dissolution of small single crystals of chiral dopants with various molecular structures 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 dependences of the rotation velocity on the helical-twisting power of the dopant and the rotational viscosity of the nematic solvent can be quantitatively described by a semi-empirical expression obtained from unit dimension considerations. The observed rotation effect can be a base for a novel method of evaluation of the 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 the molecular movement, which is closely related to the problem of molecular motors.

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