

## Rotation of small crystals of non-chiral substances at the top of a cholesteric droplet: an inverse case of the Lehmann-type effect

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Recently, a Lehmann-type effect of rotation of small single crystals of chiral substances during their dissolution at the top of a nematic droplet has been reported, with the angular velocity of rotation of the dissolving crystals of the same size being proportional to the helical twisting power of the dopant and rotational viscosity of the nematic solvent. In this paper, an inverse effect is reported — rotation of small single crystals of non-chiral substances during their dissolution at the top of a cholesteric liquid crystal matrix. The most important feature, i.e., direct proportionality of the rotation angular velocity to the degree of helical twisting, remains the same in this variant of the experiments, thus further supporting the idea that we deal with a direct evidence of transformation of the energy of chiral interactions into the energy of molecular movement. An important note is that the anisometry of the dopant is not relevant for this effect, with essentially similar results obtained for *trans*-stilbene and imidazole.

Недавно был выявлен эффект, подобный эффекту Лемана — вращение кристалликов хиральных веществ при их растворении на поверхности капли нематического жидкого кристалла; при этом угловая скорость вращения кристалликов одинакового размера пропорциональна закручивающей способности добавки и вращательной вязкости нематического растворителя. В данной работе описан обратный случай — вращение кристалликов нехиральных веществ при их растворении в холестерической жидкокристаллической матрице. Важнейшая особенность — прямая пропорциональность угловой скорости вращения степени спирального закручивания — сохраняется и в этом варианте эксперимента, подтверждая предположение о том, что в обоих случаях происходит превращение энергии хиральных взаимодействий в энергию молекулярного движения. При этом молекулярная анизометрия добавки не является существенной — близкие результаты получены для *транс*-стильбена и имидазола.

Some years ago, we reported the phenomenon of the visually observed rotational motion of a small steroid single crystal on a nematic droplet during its dissolution and accompanying induction of the cholesteric phase [1, 2]. 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 our subsequent works, our studies of the effect of rotation of single crystal of chiral dopants at the top of a nematic droplet were extended to include a number of chiral substances of different chemical nature and different helical twisting power (HTP) values (including non-chiral sub-

stances), nematic solvents with different macroscopic properties, as well as effects of the size of the dissolved crystal and the temperature of the nematic matrix [3–5]. An important and somewhat unexpected result of these studies showed that the angular velocity of rotation of the dissolving crystals was directly proportional to the helical twisting power of the dopant and to the rotational viscosity of the nematic matrix. These relationships held as quantitative dependences with the same fitting coefficient  $a$  in a rather broad range of crystal sizes, with the reciprocal crystal length at the level of 0.1–1  $\mu\text{m}$  serving as just another parameter to which the rotation velocity was proportional [4]. And, if rotational viscosity was varied not by changing the nematic matrix, but by increasing or decreasing its temperature, the angular rotation velocity changed correspondingly [5]. The general expression for the angular rotational velocity  $\omega$ , as formulated and experimentally verified in [3–5], is

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

where  $\beta$  is the helical twisting power of the chiral substance involved,  $\rho$  and  $\gamma_1$  are the density and the rotational viscosity of the liquid crystal, and  $l$  is a characteristic dimension of the crystal surface contacting the liquid crystal droplet. Thus, we claimed in these papers [3–5] that this rotation effect studied was, 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.

To generalize our approach, it was interesting to study an inverse situation — when the dissolved crystal is not chiral, and the chirality resides in the liquid crystal medium, i.e., when the crystal is dissolved on the top of a droplet of a cholesteric (i.e., helically twisted nematic).

The cholesteric matrix used in our experiments was a mixture of cholesteryl chloride (CC) and 4-octyloxy-4'-cyanobiphenyl (8OCB) taken in 1:1 mass proportion. This composition has been widely used in many works (among the latest examples, one can note the paper [6] and references therein) as a so-called "compensated" cholesteric mixture — the temperature-dependent helical twisting is of opposite signs below and above a "compensation point", and unwind-

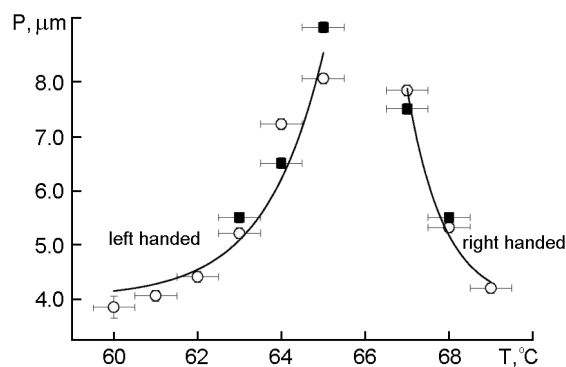


Fig. 1. Helical pitch of the cholesteric mixture CC + 8OCB as function of temperature measured by the Cano wedge method. Open and solid circles refer to two independently prepared mixture samples.

ing of the cholesteric helix is observed when this point is approached from either side. The temperature range of the cholesteric phase of this mixture, as determined by differential scanning calorimetry (Mettler TA 3000), was from 63° to 69.5°C, with substantial supercooling and relatively high stability of the supercooled state; this allowed multiple reproducible measurements in a temperature range covering lower temperatures. The helical pitch values were measured by the Cano wedge method (Fig. 1).

The non-chiral substances dissolved at the top of CC + 8OCB cholesteric droplets included imidazole and *trans*-stilbene. In both cases, small single crystals in the size range from 0.1 to 2 mm were available. The two substances are substantially different in their chemical structure from the viewpoint of molecular anisometry and potential mesomorphism — the imidazole molecule is just a five-atom heterocyclic ring, while stilbene molecule is clearly anisometric shape, and many well-known typical mesogens are among stilbene *p*-substituents [7, 8].

The angular velocity  $\gamma_a$  of the dissolving crystal was determined visually using an optical microscope. The experimental set-up and details of the experimental procedure were the same as in our previous works [3–5]. Fig. 2 shows the  $\gamma_a$  of rotation for imidazole crystals of different size measured at two temperatures: 64°C and 68°C. Similarly to the case of chiral substances [3–5] and in agreement with Eq.(1), the angular velocity was inversely proportional to the crystal length (the largest dimension) within the 0.1 mm to ~2 mm range (the other dimensions of the crystal samples cho-

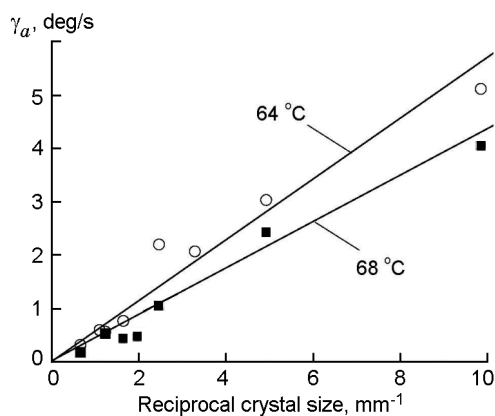


Fig. 2. Angular rotation velocity of the dissolved imidazole crystals as function of the crystal length measured at two temperatures below and above the compensation point (64°C, left-handed helix, and 68°C, right-handed helix, respectively).

sen for this set of measurements were roughly close to  $\sim 0.1$  mm). At 64°C (left-handed helix), the crystal rotation was counterclockwise; at 68°C, the clockwise rotation corresponded to the right-handed helix. A small discrepancy could be noted between linear fits for data obtained at these temperatures — the absolute values of angular velocity at 68°C were slightly but clearly lower, which could be naturally attributed to the rotational viscosity decreasing with temperature [5].

In Fig. 3,  $\gamma_a$  for imidazole and *trans*-stilbene crystals is shown as function of the reciprocal helical pitch of the CC + 80CB mixture. Accounting for the dependence of the angular velocity upon crystal size (Fig. 2), the data given were obtained for crystals of dimensions  $0.2 \times 0.1$  mm<sup>2</sup>. The helical pitch values corresponding to the measurement temperatures were taken from Fig. 1.

It can be seen that the reciprocal pitch of the helically twisted matrix in which a non-chiral crystal is dissolved effectively plays the role of helical twisting power of a chiral crystal dissolved in a nematic matrix; in both cases, Eq.(1) gives a basic description of the phenomenon of crystal rotation.

This similarity of quantitative description supports the idea that in both cases — chiral crystal in non-chiral matrix or non-chiral crystal in chiral matrix — we see a direct evidence of transformation of the energy of chiral intermolecular interactions into the energy of molecular movement. This phenomenon can also be considered as another example of chirality transfer [9] — from the microscopic to the macroscopic

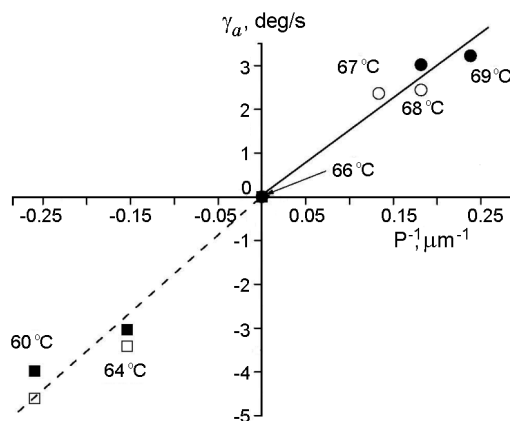


Fig. 3. Angular rotation velocity of the dissolved imidazole (open circles/squares) and *trans*-stilbene (solid circles/squares) as function of the inverse helical pitch of the cholesteric mixture. Squares and circles refer to counterclockwise and clockwise rotation, respectively. The solid and dashed lines are linear fits for points above and below the compensation point (where no rotation was observed).

level (the case of [1–5]) or from the mesoscopic (structural) level to the macroscopic level (the present work).

Another important point is essential similarity of the results obtained for *trans*-stilbene and imidazole. This suggests that molecular structure features of the dopant (including anisotropy) are not relevant for this effect — in the same way as the chiral dopant nature was irrelevant in the previous case [3–5]. This allows us to assume that the phenomenon studied is of purely "physical" nature, with any specific interactions between the dopant and matrix molecules being of minor importance.

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## **Обертання кристаликів нехіральних речовин на холестеричній краплині: обернений випадок ефекту леманівського типу**

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Нещодавно було виявлено ефект, подібний до ефекту Лемана, який полягає в обертанні кристаликів хіральних речовин при їх розчиненні на поверхні краплини нематичного рідкого кристала, кутова швидкість обертання кристаликів однакового розміру пропорційна закручувальній здатності домішки та в'язкості нематичного розчинника. В цій роботі описано зворотній ефект — обертання кристаликів нехіральних речовин при їх розчиненні у холестеричній рідкокристалічній матриці. Найважливіша риса, тобто пряма пропорційність кутової швидкості обертання ступеня спірального закручування, зберігається і в цьому варіанті експерименту, підтверджуючи висновок про те, що в обох випадках ми маємо пряме свідчення перетворення енергії хіральних взаємодій в енергію молекулярного руху. Важливою особливістю є те, що молекулярна анізотропія домішки не є істотною у цьому ефекті — істотно подібні результати отримано для *транс*-стильбену та імідазолу.