

Helical twisting in cholesterics doped by banana-shaped molecules

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Helical pitch vs. temperature measurements were carried out for cholesteric liquid crystal matrices of different types doped with a set of banana-shaped compounds. The effects of these dopants on the helical pitch were found to be essentially different for systems based on cholesterol esters and for induced cholesterics based on twisted nematics. In the first case, all the dopants used decreased the helical pitch, i.e., caused additional helical twisting, with its magnitude varying for different dopants. In the second case, with matrices based on chiral R-811 and S-811 in cyclohexanecarboxylic acids (CHCA) and 5CB, unwinding of the helix was generally observed. For one of the dopants, however, namely, for 1-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-3-[4-(4-nonylbenzoyloxy)benzoyloxy] benzene, additional twisting was noted in matrices with CHCA close to the isotropic transition point, and in matrices with 5CB — in all the temperature range. The results obtained can be considered as important arguments in the controversial issue of chiral properties of banana-shaped compounds in liquid crystal phases.

Определены зависимости шага спирали от температуры для холестерических матриц различных типов, легированных рядом добавок с молекулами банановидной формы. Установлено, что влияние этих добавок на шаг спирали существенно отличается для систем на основе эфиров холестерина и для индуцированных холестериков на основе закрученных нематиков. В первом случае все добавки приводили к уменьшению шага спирали, т.е. вызывали дополнительное закручивание. Во втором случае, с матрицами на основе хиральных R-811 и S-811 в циклогексанкарбоновых кислотах (ЦГКК) и 5CB, наблюдалось раскручивание спирали. В то же время для одной из добавок, а именно, 1-[4-(4-додецилоксibenзоилокси)бензоилокси]-3-[4-(4-нонилбензоилокси)бензоилокси] бензола, отмечено дополнительное закручивание в матрицах с ЦГКК вблизи точки изотропного перехода, а в матрицах с 5CB — во всем температурном интервале. Полученные результаты можно рассматривать как важный аргумент в противоречивом вопросе о хиральных свойствах бананоподобных веществ в жидкокристаллических фазах.

1. Introduction

Among the new challenging objects of liquid crystal (LC) science, one can note so-called "bent-core" or "banana-shaped" molecules, which, either forming LC phases by themselves or acting as dopants in various LC matrices, give rise to a number of peculiar features of the mesomorphic properties

[1, 2]. The most intriguing of these features is that, though banana-shaped molecules are not chiral (i.e., show no optical activity), they can induce chiral properties in liquid crystalline phases [3, 4]. Thus, smectic layers formed by such molecules can possess both chirality and polarity, resulting in ferroelectric and antiferroelectric LC phases essentially similar formed by well-known

Table.

Dopant No.	Chemical formula	Phase transition temperatures
1		Cr-(76.2°C) → SmB ₂ -(80.4°C) → I
2		Cr-(97.6°C) → SmB ₂ -(133°C) → I
3		Cr-(121°C) → SmB ₂ -(153°C) → I
4		Cr-(69°C) → SmB ₂ -(110°C) → I
5		Cr-(60.9°C) → SmB ₁ -(79.8°C) → N-(80.4°C) → I

chiral smectics-C*. Moreover, doping of a chiral ferroelectric liquid crystal with an achiral bent-core molecule can enhance the chirality of the system irrespective of the handedness of the host [5]. Even macroscopically isotropic liquids formed by banana-shaped molecules can display signs of chirality due to the presence of short-range smectic-like positional order; in such systems, the only macroscopically broken symmetry is chirality [6].

It has been reported [7] that doping of chiral nematic (cholesteric) liquid crystals with achiral banana-shaped dopants can enhance helical twisting, which is manifested by a decrease in helical pitch (determined by measurements of selective reflection spectra). This was explained by an assumption that achiral molecules possessing equal and opposite chiral conformations with high helical twist, when placed in chiral environment, preferentially assume the conformation that favors twisting of the same sense as the twisting of the host phase [8].

There are numerous publications on chiral properties of banana-shaped molecules, but practically all of them deal with smectic phases. On the contrary, data related to nematic and cholesteric phases are scarce and inconclusive [9].

In our work, we studied a set of five different banana-shaped molecules as dopants in cholesteric matrices of different

chemical composition. Our aim was to distinguish between purely physical factors and effects of intermolecular interaction features that could be specific to certain types of systems.

2. Results and discussion

Chemical structure of the banana-shaped molecules and mesomorphic transition points of LC phases formed by these substances are shown in Table. Banana-shaped compounds are known to form seven modifications of biaxial smectic mesophase [10], with the eighth modification described in [1]. Chiral properties are shown by compounds forming B₂ (SmCP) mesophase with ferroelectric properties. Thus, compound No.2 (Table), which contains bromine atom only in the central naphthalene fragment, forms ferroelectric mesophase of modification B₂ [11]. When bromine is present in aromatic rings of lateral fragments, the ability of 2,7-dihydroxynaphthalene esters to form the ferroelectric B₂ mesophase is weakened, and compound No.5, which, like compound No.2, includes terminal dodecyloxy groups, is characterized by formation of the nematic and B₁ (Col_v) phases. The induced B₂ phase is observed only in the electric field [12]. The compound No.1, which contains chlorine atoms in lateral fragments [13], differs from its bromine-containing analog (compound No.5) by the

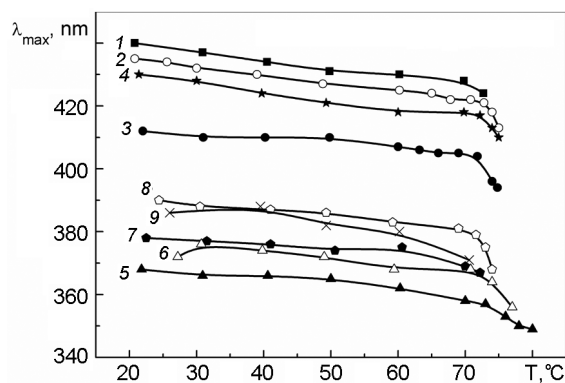


Fig. 1. Selective reflection maximum λ_{max} as function of temperature for cholesteric systems with banana-shaped dopants: 1 — M5, 2 — M5 + 1 % No.2, 3 — M5 + 5 % No.2, 4 — M5 + 1 % No.3, 5 — M5 + 10 % No.1, 6 — M5 + 7 % No.1, 7 — M5 + 10 % No.5, 8 — M5 + 7 % No.5, 9 — M5 + 7 % No.4.

presence of B_2 phase without electric field. Synthesis and mesomorphic properties of 1,3-dihydroxyphenol with different number of benzene rings in lateral chains (compound No.3) or with different terminal groups (compound No.4) were presented in [14].

Three cholesteric LC hosts were used:

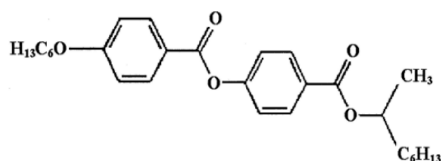
1. Steroid cholesteric matrix M5 (65 % cholesterylnonanoate + 30 % cholesterylformate + 5M % cholesterylbutyrate);

2. Induced cholesteric matrix (25 % S-811 or R-811 + 75 % 4CHCA (4-*trans*-butyl-cyclohexanecarboxylic acid);

3. Another induced cholesteric matrix (25 % S-811 + 75 % 5CB (4-pentyl-4'-cyanobiphenyl).

S-811 and R-811 (obtained from Merck) are chiral dopants of opposite chirality:

Selective reflection (SR) spectra were measured using a Hitachi 330 spectrophotometer; the cholesteric mixture in the



isotropic phase was introduced into a thermostabilized 10 μm thick cell by capillary forces; the cell walls were pre-treated with PVA and unidirectionally rubbed, which ensured formation of planar texture. The detailed procedure of sample preparation and measurements was described in [15]. The SR maximum wavelength λ_{max} was, as it is conventional for cholesteric

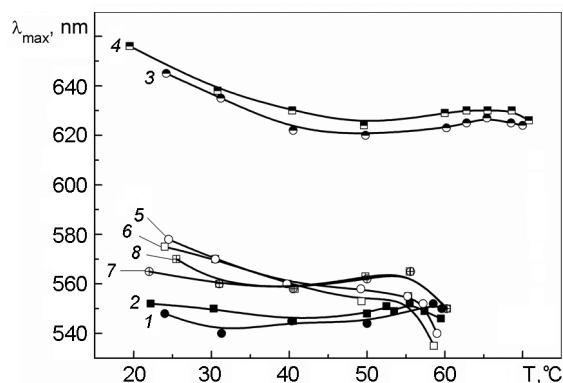


Fig. 2. Selective reflection maximum λ_{max} as function of temperature for induced cholesteric systems: 1 — 25 % R-811 + 75 % 4-CHCA, 2 — 25 % S-811 + 75 % 4-CHCA, 3 — 22.5 % R-811 + 67.5 % 4-CHCA + 10 % No.1, 4 — 22.5 % S-811 + 67.5 % 4-CHCA + 10 % No.1, 5 — 23.25 % R-811 + 69.75 % 4-CHCA + 7 % No.4, 6 — 23.25 % S-811 + 69.75 % 4-CHCA + 7 % No.4, 7 — 22.5 % R-811 + 67.5 % 4-CHCA + 10 % No.5, 8 — 22.5 % S-811 + 67.5 % 4-CHCA + 10 % No.5.

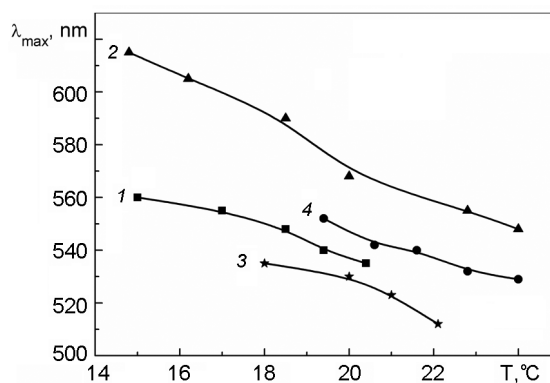


Fig. 3. Selective reflection maximum λ_{max} as function of temperature for induced cholesteric systems: 1 — 25 % S-811 + 75 % 5CB, 2 — 22.5 % S-811 + 67.5 % 5CB + 10 % No.1, 3 — 23.25 % S-811 + 69.75 % 5CB + 7 % No.4, 4 — 22.5 % S-811 + 67.5 % 5CB + 10 % No.5.

liquid crystals, considered as a measure of helical pitch p ($\lambda_{max} = np$, where n is the refractive index); the value of λ_{max} is often called "the optical pitch" (see, e.g., [7]). The helical twisting is determined by the inverse pitch p^{-1} , thus, from our data we evaluated changes in $1/\lambda_{max}$ as function of the dopant mass concentration C .

The results on λ_{max} as function of temperature for the three types of cholesteric matrices are presented in Figs. 1–3. The shifts of inverse optical pitch values as

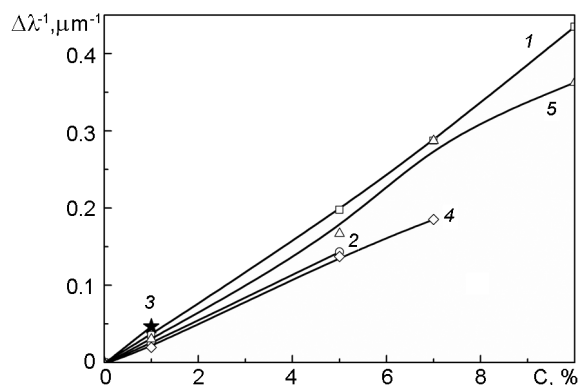


Fig. 4. Recorded changes in $1/\lambda_{max}$ as function of concentration C of banana-shaped compounds: 1 — M5 + No.1, 2 — M5 + No.2, 3 — M5 + No.3, 4 — M5 + No.4, 5 — M5 + No.5.

function of banana-shaped dopant concentration are shown in Figs. 4, 5.

All the dopants Nos.1–5 induce additional helical twisting in the steroid cholesteric mesophase (matrix M5, Figs. 1 and 4). This effect is the strongest with dopant No.1, and the weakest — with dopant No.4. Dopant No.3 is rather close to No.1 in this respect (though its solubility was the lowest, and measurements were possible only at concentrations below ~1 %). Dopant No.2 is close to No.4.

In non-steroid matrices (nematic + chiral dopant), the observed behavior was essentially different. In the S-811 + 4CHCA and R-811 + 4CHCA hosts (Fig. 2), all the dopants led to untwisting of the cholesteric helix (as it could be normally expected non-chiral dopants). It should be noted that with S-811 and R-811 (enantiomers of opposite chiralities) the measured values of $\lambda_{max}(T)$ and their dopant-induced shifts were nearly the same within experimental errors (though the helical twisting was of opposite senses). It should be noted that the weakest untwisting was noted for dopants No.4 and No.5.

An obvious conclusion is that the character of dopant-induced changes in helical twisting is not directly related to specific features of banana-shaped molecules and is essentially determined by the chemical nature of the cholesteric host. Enhancement of twisting by non-chiral dopants (e.g., conventional nematics) is well known for steroid cholesteric matrices (i.e., based on cholesterol esters). On molecular level, this is explained by steric interaction between the steroid ring ("angular" methyl groups stretching out of the basic plane) and an-

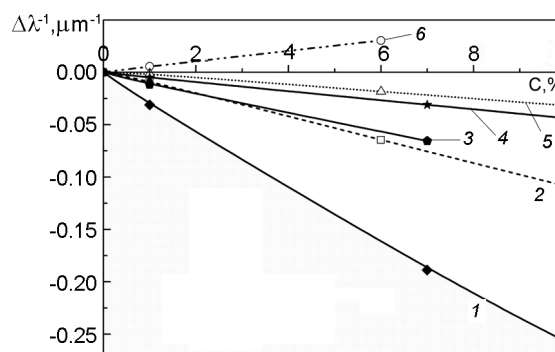


Fig. 5. Recorded changes in $1/\lambda_{max}$ as function of concentration C of banana-shaped compounds: 1 — (25 % S-811 + 75 % 4-CHCA) + No.1, 2 — (25 % S-811 + 75 % 5CB) + No.1, 3 — (25 % S-811 + 75 % 4-CHCA) + No.4, 4 — (25 % S-811 + 75 % 4-CHCA) + No.5, 5 — (25 % S-811 + 75 % 5CB) + No.5, 6 — (25 % S-811 + 75 % 5CB) + No.4

isotropic (elongated) molecules of the dopant [16, 17]). With a non-steroid cholesteric host, the effect of twisting enhancement if present at all, is much weaker than the normal untwisting caused by addition of non-chiral components to the cholesteric system.

In this respect, one should note that in the frequently cited work [7] the effect of anomalous twisting by banana-shaped molecules was observed in the cholesteric phase of cholesteryl 4-formylbenzoate, and no reliable data could be found on similar effects in induced (non-steroid) cholesterics.

Of course, there is some contribution of the "banana-like" shape to helical twisting changes upon doping. We see that dopant No.4 leads to the weakest untwisting (and even some twisting can be noted close to the isotropic transition). Moreover, when we use induced cholesterics based on nematic 5CB (Fig. 3), dopant No.4 really gives rise to extra twisting. This, however, can be related to other features of cyanobiphenyl-based induced cholesterics, presumably due to dimer formation and pre-transitional phenomena in a broad temperature range.

Further discussion and theoretical assessment should probably involve data on cholesterics doped with azoxy nematics assuming stable *cis*-form under UV irradiation [15, 18]. In this case, it was argued that molecular structure of azoxy nematic molecules in *cis*-form could be considered as geometrically similar to conventional "bent-

core" molecules. Future experimental studies (now under way) would include other examples of bent-core molecules, as well as other cholesteric matrices with different chemical composition.

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Спіральне закручування у холестериках, допованих бананоподібними молекулами

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Визначено залежності кроку спіралі від температури для холестеричних рідкокристалічних матриць різного типу, допованих низкою молекул бананоподібної форми. Установлено, що вплив цих допантів на крок спіралі істотно відрізняється для систем на основі естерів холестерину та для індукованих холестериків на основі закручених нематиків. У першому випадку всі допанти призводили до зменшення кроку спіралі, тобто спричиняли додаткове закручування, ступінь якого варіювала для різних допантів. У другому випадку, з матрицями на основі хіральных R-811 та S-811 у циклогексанкарбонових кислотах (ЦГКК) та 5CB спостерігалось розкручування спіралі. Проте, для одного з допантів, а саме, 1-[4-(4-додецилоксибензоїлокси)бензоїлокси]-3-[4-(4-нонілбензоїлокси)бензоїлокси]бензолу, відзначено додаткове закручування у матрицях з ЦГКК поблизу точки ізотропного переходу, а у матрицях з 5CB — в усьому інтервалі температур. Отримані результати можна розглядати як важливий аргумент у суперечливому питанні хіральных властивостей бананоподібних речовин у рідкокристалічних фазах.