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Cholesteric Liquid Crystals Doped with Molecules of Organic Scintillator Materials

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Effects on mesomorphic properties and selective reflection of cholesteric matrices have been studied for a special group of non-mesogenic dopants – organic luminophores that are actually or potentially used as organic scintillator crystals (stilbene, p-terphenyl, o-POPOP and other substances with similar features). Solubility of these compounds in cholesteric solvents, as well as their influence on isotropic transition temperatures and helical twisting, were substantially different for different dopants and matrices. The characteristics of these effects are shown to be dependent on the degree of anisometry of solvent molecules, as well as their specific interactions with components of the solvents.

Keywords: cholesteric-isotropic transition; cholesteric liquid crystals; helical twisting; non-mesogenic dopants; organic scintillators

INTRODUCTION

Many new and promising applications of cholesteric liquid crystals (CLC) are stipulated by peculiar properties of non-mesogenic dopants (NMD) that can be introduced into the cholesteric matrix. One can mention luminescent dye-doped CLC displays, with their performance essentially dependent on absorption and emission characteristics of the dopant [1], bioequivalent detectors of UV radiation based on CLC doped with a photosensitive substance of biological origin (e.g., provitamin D) [2,3], as well as works on lasing in dye-doped CLC [4–6]. The growing general interest in nanotechnologies and nanostructured objects suggest a search for systems where NMD in CLC

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would be present in the form of supramolecular aggregates, which could lead to new unexpected phenomena. An inspiring prompt could come from specific properties of aggregated aromatic chromophores in a soft matter-like state, where unusual luminescent properties were reported, such as unusual eximer emission of pyrene [7,8].

In our work, we used several well-known organic compounds that had been widely used as basic components of functional materials (e.g., organic scintillator crystals) as non-mesogenic solutes in cholesteric mixtures containing components of different chemical nature. Our primary aim was to determine the effects of these substances used as NMDs upon thermal stability and helical twisting of CLC, finding out and explaining possible deviations and differences related to peculiar features of molecular structure and intermolecular interactions.

MATERIALS AND METHODS

We used cholesteric matrices of three different types, i.e., mixtures of cholesteryl esters, nematic-cholesteric mixtures containing both steroid and non-steroid components, and induced cholesterics formed by nematics with non-steroid chiral dopants. The matrices used were chosen to ensure the selective reflection maximums well outside the dopant absorption bands.

Matrix M15 is a multi-component mixture containing 26% cholesteryl nonanoate, 12% cholestery formate, 2% cholesteryl butyrate and 60% of a non-aromatic nematic component – 4-*trans*-butyl-cyclohexanecarboxylic acid (4CHCA). The cholesterol esters were produced by Chemical Reagents Plant, Kharkov, Ukraine, and 4CHCA – by NIOPIK, Russia. This matrix showed a slight increase in helical pitch with temperature ($d\lambda_{\max}/dT > 0$).

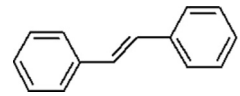
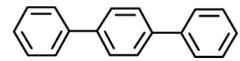
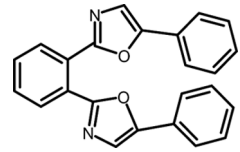
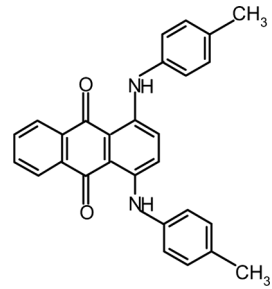
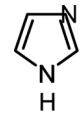
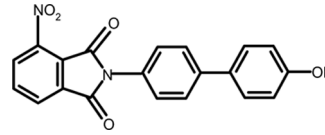
Matrix M5 contained only cholesterol esters – cholesteryl nonanoate (65%), cholesteryl formate (30%) and cholesteryl butyrate (5%).

Matrix M19 is a nematic mixture of alkyl- and alkoxycyanobiphenyls (ZhK-1282, NIOPIK, Russia) containing 33% of optically active dopant 4-(2-methylbutyl)-4′-cyanobiphenyl (CB15, Merck, Germany).

The substances used as non-mesogenic dopants are listed in Table 1. Stilbene and *p*-terphenyl are widely used in the form of scintillator crystals; *o*-POPOP is also promising for such applications. Many imidazole derivatives are known as organic luminophores; the other two substances, used in some comparative experiments, are examples of organic dyes and semiconductors.

The selective reflection bands were determined from optical transmission spectra measured in a 20 micron thick cell using a

TABLE 1 Substances Used as Non-Mesogenic Dopants to Cholesteric Matrices

Compound	Chemical structure
Stilbene	
p-terphenyl	
o-POPOP	
N,N′-(4-methylphenyl)-1,4-diaminoanthraquinone (AQ)	
Imidazole	
2-nitrophtalimido-4′-oxydiphenyl (NFTD)	

Hitachi 330 spectrophotometer. The appropriate quantity of NMD substance was dissolved in the cholesteric matrix in the state of isotropic liquid, and the mixture obtained was introduced between the measurement cell walls by capillary forces. Before introduction of the mixture into the cell, the cell walls were immersed in a 0.5% water solution of polyvinyl alcohol, dried and rubbed in one direction by a soft tissue, ensuring good planar texture with clear and reproducible selective reflection peaks.

Cholesteric-isotropic phase transition temperatures were determined by differential scanning calorimetry (DSC) using a Mettler TA3000 thermoanalytical system and checked by polarization microscopy.

RESULTS AND DISCUSSION

The measured wavelengths of maximum selective reflection λ_{max} as function of temperature and concentration of stilbene, p-terphenyl and o-POPOP in M15 are shown in Figure 1(a–c). Figure 1(d) shows λ_{max} as function of dopant concentration at a specified temperature (40°C). All three solutes lead to helix unwinding (λ_{max} increases). The largest effect on λ_{max} was caused by stilbene, with the shift of ~60 nm at ~5%. *o*-POPOP, though well soluble at least to concentrations of 10%, giving well defined selective reflection peaks, did not cause significant changes in λ_{max}. *p*-Terphenyl,

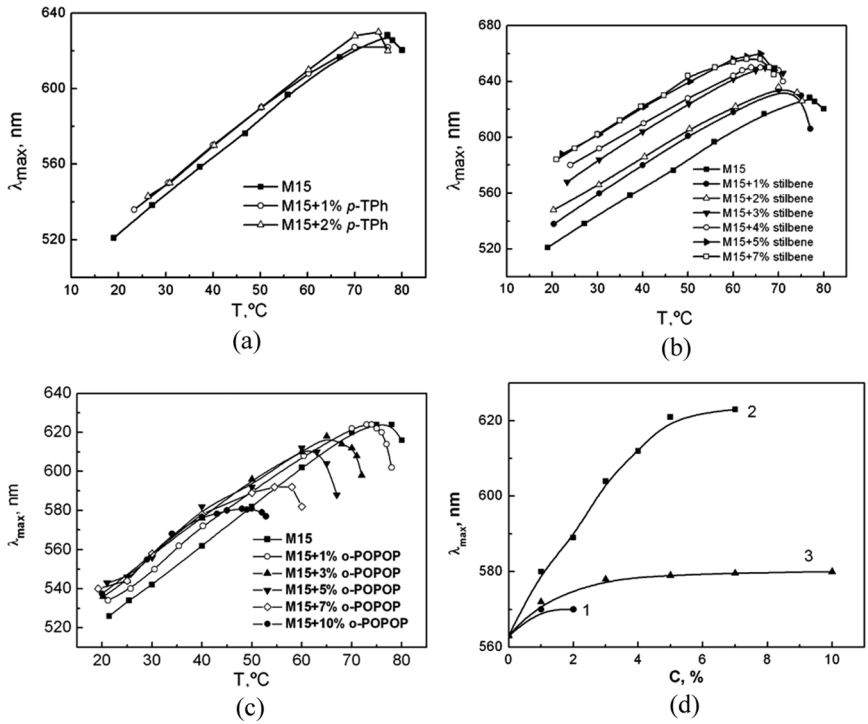


FIGURE 1 Wavelength of maximum selective reflection λ_{max} as function of temperature (a–c) and NMD concentration at 40°C (d) in cholesteric mixture M15 doped with *p*-terphenyl (a), stilbene (b) and *o*-POPOP (c).

incorporating into the matrix only at very small concentrations, also shifted λ_{max} weakly.

Evaluation of eutectic coordinates using Schroeder-van Laar equations give the following values for eutectic concentrations in cholesteryl myristate: for *o*-POPOP C ~ 21%, for stilbene C ~ 9%, for *p*-terphenyl C ~ 1%, which is in agreement with our experimental estimates of solubility.

Figure 2 shows λ_{max} as function of temperature for different concentrations of imidazole in different cholesteric matrices. In M19, the introduction of imidazole decreased λ_{max}; this can be naturally explained by the negative sign of $d\lambda_{max}/dT$ in this matrix – the NMD molecules worsen the orientational order, thus changing the helical pitch in the same direction as it would be changed by increasing the temperature [9]. This mechanism is similar to the

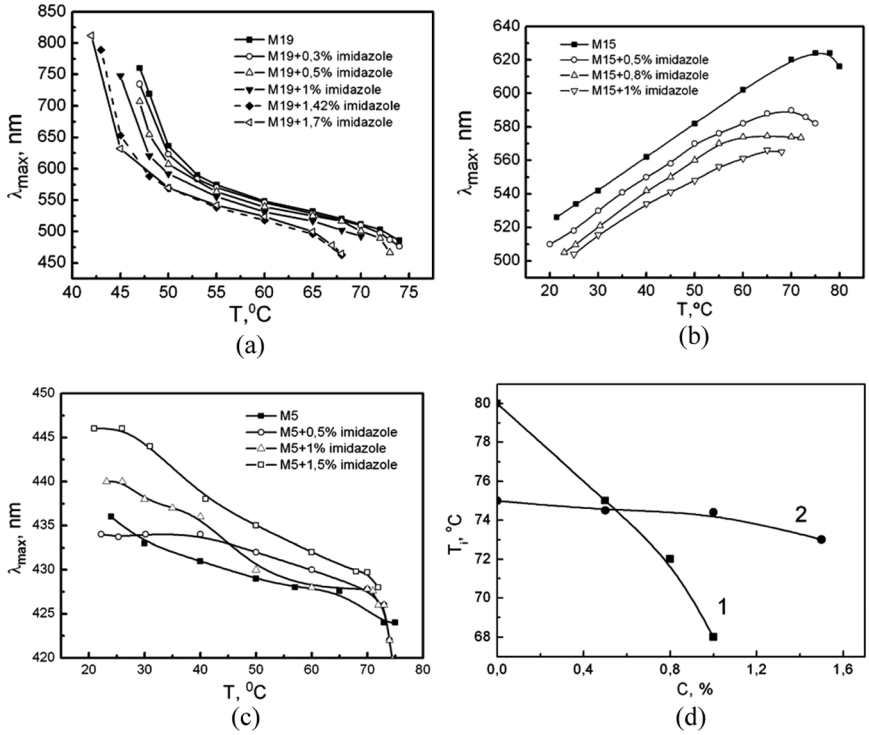


FIGURE 2 Effects of imidazole upon λ_{max} in cholesteric mixtures M19 (a), M15 (b) and M5 (c) and its effects upon cholesteric-isotropic phase transition temperature (d).

above-described case (Fig. 1), accounting for the difference in the sign of $d\lambda_{max}/dT$ in M19 and M15. However, if we use M15 as a solvent for imidazole, the picture becomes essentially different – imidazole, which is not chiral and non-mesogenic, induces further helical twisting with λ_{max} decreasing in a matrix with positive $d\lambda_{max}/dT$. Since the molecule of imidazole is not anisometric, we can not apply the reasoning that explained the appearance of additional twisting in nematic-cholesteric mixtures [9].

To understand the situation, we carried out an additional experiment using Matrix M5, composed only of cholesterol esters without any non-steroid components (Fig. 2c). In this case, imidazole acted as a typical non-chiral component, leading to an increase in λ_{max} even while λ_{max} slightly decreased with temperature). In addition to its unusual effects on helical twisting, imidazole also affected the cholesteric-isotropic transition temperatures of M15 and M5 in substantially different ways (Fig. 2d).

This peculiar behavior of imidazole can be explained by its specific interaction with carboxylic acid molecules (4CHCA) that are present in M15. Some of the 4CHCA dimers dissociate into individual molecules, which interact with imidazole forming rather stable imidazole-carboxylic acid complexes [10]. As a result, particles of much lower anisometry than cholesterol esters and 4CHCA dimers are formed, which decreases the orientational order and lowers the isotropic transition temperature, and the newly formed structures appear to favor the helical twisting.

Another NMD studied in this context was NFTD (Fig. 3). Its behavior was generally similar to stilbene, *p*-terphenyl and *o*-POPOP; as a peculiar feature, one can note its low solubility and much weaker effects on both cholesteric-isotropic transition temperature and selective reflection spectra as compared with other solutes at comparable concentrations.

The effects of NMD introduction upon thermal stability of the cholesteric mesophase are summarized in Figure 4. The data presented refer to Matrix M15. (For comparison, data are also shown that were obtained for yet another interesting dopant – N,N′-(4-methylphenyl)-1,4-diaminoanthraquinone (AQ) [11,12]; the composition of Matrix M18 used in these measurements was essentially similar to M15, with some variation in the percentage of the same components).

One of the main parameters of NMD that determine the application prospects of the doped cholesteric system is the NMD solubility in the cholesteric matrix. Thus, *p*-terphenyl and NFTD have low solubility ($\sim$1% and $\sim$2%, respectively); however, NFTD is distinguished by its

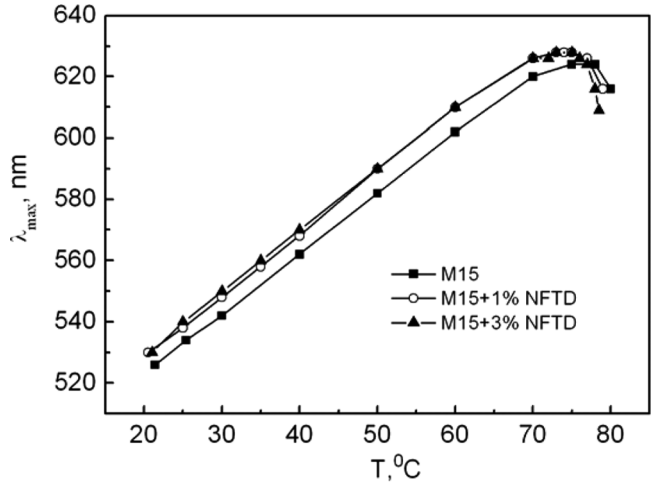


FIGURE 3 λ_{max} as function of temperature and concentration of NFTD in cholesteric mixture M15.

very weak influence upon thermal stability (dT_i/dC is very small). On the other hand, *o*-POPOP shows unusually high solubility (no signs of dopant precipitation up to ~10% and more), while its effect upon helical twisting is very weak as compared, e.g., with stilbene, which has noticeably lower solubility).

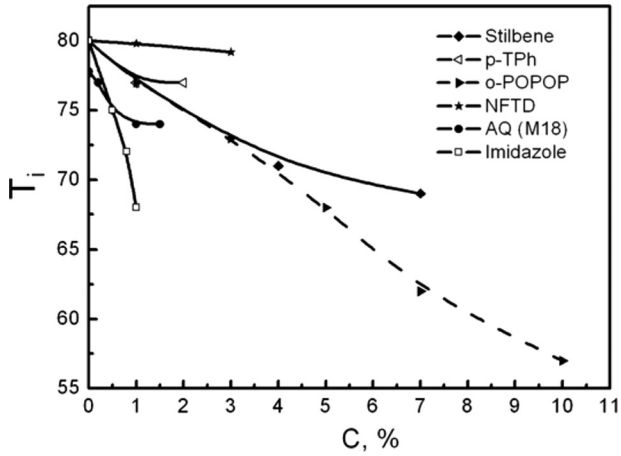


FIGURE 4 Cholesteric-isotropic phase transition temperature as function of concentration of several non-mesogenic dopants in cholesteric matrix M15.

TABLE 2 Calculated Characteristics of Molecular Anisometry*

NMD	Anisometry coefficient $\alpha=(a-b)/(a+b)$	Molecular surface area S, Å^2	Anisotropic interaction area $S_a=S\cdot\alpha$, Å^2	$-dT_i/dC$
Stilbene	0.33	350.5	114.0	3.0
p-terphenyl	0.43	370.7	158.9	2.8
o-POPOP	<0.01	432.8	1.9	3.0
AQ	0.19	479.1	91.8	4.0
Imidazole	0.10	179.3	17.3	10.0
NFTD	0.36	453.2	163.8	0.2

*dT_i/dC values were determined in Matrix M15 from linear segments of $T_i(C)$ dependences close to T_i.

To get an insight into the situation, we made an attempt to establish a relationship between the NMD effect upon the degree of depression of the cholesteric-isotropic transition point (characterized by the value of dT_i/dC close to $C=0$) and the degree of anisometry of the NMD molecule. For quantitative characterization of the molecular anisometry, we used the anisometry coefficient $\alpha=(a-b)/(a+b)$ (approximating the molecular shape by an ellipsoid with axes a and

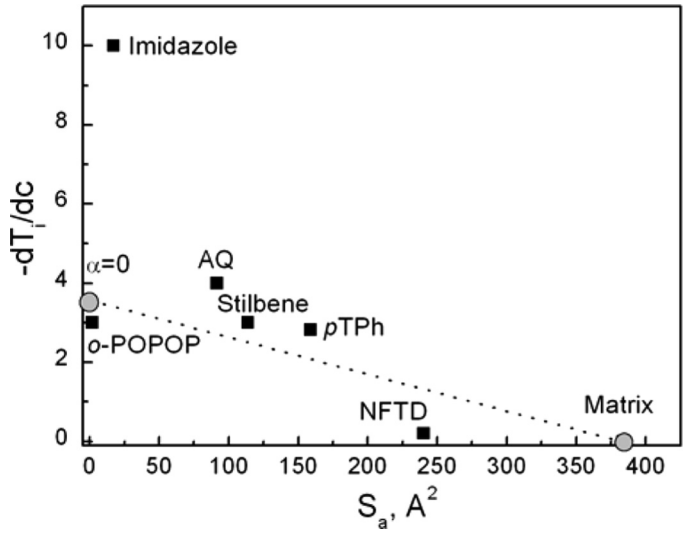


FIGURE 5 Depression of the cholesteric-isotropic transition point dT_i/dC as function of the calculated anisotropic interaction area S_a (a parameter characterizing the molecular anisometry of NMD molecules).

b) multiplied by the molecular surface area S, introducing the anisotropic interaction area $S_a = \alpha$ S [13]. The values of a, b and S were obtained using simple HyperChem-based numerical calculations. The results obtained are presented in Table 2.

Figure 5 shows the values of dT_i/dC measured in M15 for all the solutes studied as function of the calculated anisotropic interaction area S_a. The dotted line connects two "theoretical" points: "$\alpha = 0$" represents the "ideal" NMD with zero anisometry leading to extrapolated $T_i = 0$ K at 100% concentration, and the point labeled as "Matrix" corresponds to the weighted average of S_a calculated for the matrix molecules and $dT_i/dC = 0$. All dopants used in the present study fall rather close to the "ideal" behavior, with imidazole being the only exception (the imidazole molecule forms a complex with one monomer of the dimerized carboxylic acid).

CONCLUSIONS

Substances from the studied set of compounds, when used as non-mesogenic dopants in cholesteric matrices, in many cases caused non-trivial effects upon helical twisting and cholesteric-isotropic transition temperatures. In the latter case, depression of isotropic transition temperatures generally showed a clear dependence on anisometry of NMD molecules, with certain exceptions (imidazole) explained by specific interactions with components of the cholesteric matrices. As for NMD effects upon helical twisting, the theoretically predictable general picture (decreasing helical pitch due to non-chiral nature of the dopants and changes in helical pitch explained by weakening of the orientational order) could also be modified by specific intermolecular interactions. Our analysis of the data obtained presumably shows the ways to optimize the composition of cholesteric systems containing solute molecules with specified functional material properties.

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