

MOLECULAR CRYSTALS AND LIQUID CRYSTALS

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Part I of II

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Effects of Anthraquinone Dye Aggregation on Selective Reflection Spectra of Cholesteric Liquid Crystal

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The formation of supramolecular aggregates of anthraquinone dye N,N'-(4-methylphenyl)-1,4-diaminoanthraquinone (AQ) is shown to be clearly manifested in temperature-dependent selective reflection spectra of cholesteric solvents containing AQ as a non-mesogenic dopant. Using cholesteric matrices of different chemical nature (based on cholesterol esters or nematics with chiral dopants), one can distinguish between interactions of a solvent with individual AQ molecules and AQ aggregates, as well as between the aggregation and precipitation of AQ. The calculated relative birefringence data demonstrate the effects of AQ aggregates on the optical anisotropy and the orientational order in the systems under study.

Keywords: aggregation; anthraquinone dye; birefringence; cholesteric liquid crystal; non-mesogenic dopant; selective reflection

INTRODUCTION

Owing to the strong interaction, self-associated molecular aggregates possess chemical and optical properties which can differ significantly from those of individual molecules. In recent years, many efforts have been made to investigate aggregation processes and structure-property relationships of diverse molecular aggregates due to their unique physicochemical properties. An important reason for the

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strongly increased interest in molecular aggregates was their potential technological application in various fields. The self-association of molecules plays a significant role in the nature, particularly in living systems. All membranes of animal cells are based on self-assembled molecules of phospholipids which tend to aggregate in aqueous environments due to the so-called hydrophobic (water-insoluble) interaction forming molecular layers and closed structures (vesicles). In biophysics, molecular aggregates of chlorophyll have been found to mediate the primary light-harvesting and charge-transfer processes in photosynthetic units of plants [1–3]. In technological fields, molecular aggregates have been employed as potential organic photoconductors [4], as materials with enhanced nonlinear optical properties [5,6] for the use in nonlinear optics devices [7–9] and for information processing and storage [10]. They are widely used in photographic materials as antenna systems on the surface of silver halide microcrystals to collect light for the photographic process [11,12]. The importance of the aggregation for a variety of physical processes attracted the attention of many researchers and initiated numerous studies.

Despite the number of relevant studies conducted with molecular aggregates, in particular dye aggregates [13–16], the focus of these researches is still on aqueous solutions of organic molecules and is very much an art for other liquids, like liquid crystals. The aggregation of dyes in liquid crystal materials is described much less [17–20]. In [17], the crystallization of dyes into a specific form has been attributed to the dye aggregation prior to the crystallization. In [19,20], the aggregation of dye molecules is evidenced by a strongly nonlinear dependence of the polarizability $a = a_L + a'E^2$ on the dye concentration c . The nonlinear dependence $a'(c)$ indicates the domination of supramolecular units in the optical response.

Moreover, the limited number of experimental data is also motivated by the lack of methods developed to check the aggregation in solutions other than water. Since molecular aggregates can be differentiated from other molecules by their spectroscopic features, spectroscopic methods are most suitable for investigations of the formation of aggregates. However, due to the complexity of the liquid crystal environmental conditions (intense light scattering) and a possible interaction between dye and host molecules, spectroscopic measurements have only a limited value for investigations of aggregation states.

In contrast to this, we describe experimental measurements that make it possible to reveal the dye aggregation in a cholesteric liquid crystal solvent by a characteristic selective light reflection shift of cholesteric materials, which is much more sensitive to changes in

the aggregation state than the spectral characteristics of an aggregate itself for systems based on liquid crystals. Thus, the measurements executed in the present paper allow us to detect and to follow up the changes in the aggregation state of dye molecules in a liquid crystal solvent.

MATERIALS AND METHODS

In our experiments, we used N,N'-(4-methylphenyl)-1,4-diaminoanthraquinone (AQ) as a non-mesogenic dopant. AQ is a typical example of anthraquinone dyes, and it was extensively studied in nematic matrices from the viewpoint of non-linear optics [19,21].

We used cholesteric matrices of two different types, i.e., cholesterics based on cholesterol derivatives and induced cholesterics formed by nematics with optically active dopants (OAD). The used matrices were chosen to ensure the selective reflection maximum well outside the AQ absorption bands.

The first matrix (M18) is a multicomponent mixture comprising 32.5% cholesteryl nonanoate, 15% cholesteryl formate, 2.5% cholesteryl butyrate and 50% of a non-aromatic nematic component—4-*trans*-butyl-cyclohexanecarboxylic acid (4CHCA). The cholesterol esters were produced by Chemical Reagents Plant, Kharkiv, Ukraine, and 4CHCA was bought from NIOPIK, Russia. This matrix showed a slight increase in the helical pitch with temperature ($d\lambda_{\max}/dT > 0$).

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). This matrix does not contain steroid components, which allowed us to exclude possible interaction effects of AQ molecules with the steroid ring. In M19, $d\lambda_{\max}/dT$ is negative, and the helix sense (right-handed) is also opposite to that of M18 (left-handed).

The appropriate quantity of AQ was dissolved in the cholesteric matrix in the state of isotropic liquid. The cells were assembled from pairs of glass substrates covered with polyvinyl alcohol and with rubbing directions being antiparallel to each other. The thickness of the gap between the glass plates in the LC cells was measured by the interference technique prior to the filling. The cells were filled at a temperature of about 10°C above the clearing point by the capillary flow assisted by negative pressure, and then promptly sealed. The selective reflection bands were determined from the optical transmission spectra measured in a 20- μm thick cell using a Hitachi 330 spectrophotometer.

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RESULTS AND DISCUSSION

The measured wavelengths of maximum selective reflection λ_{\max} as functions of the temperature and the AQ concentration in M18 are shown in Figure 1.

One can see that increasing the AQ concentration up to 1% gives rise to the additional helical twisting which results in decreasing λ_{\max} . Since $d\lambda_{\max}/dT > 0$, this cannot be explained by a decrease in the orientational order, which should lead to increasing the reflection maximum as caused by increase in the temperature. At higher AQ concentrations ($\sim 1.5\%$), the character of the dopant effects is essentially dependent upon the temperature—at relatively lower temperatures (25–50°C), the helical pitch (λ_{\max}) decreases (with respect to the initial matrix), while, at higher temperatures (50–70°C), it increases (Fig. 2). Thus, the effect of “additional” twisting of the cholesteric helix caused by AQ dopants disappears close to T_i at higher AQ concentrations.

Since an AQ molecule is not chiral, the induction of the additional helical twisting in the studied M18 + AQ systems should be due to the same type of steric interactions which lead to the extra helical twisting in nematic-cholesteric mixtures [22]. It can be assumed that, at higher AQ concentrations (1.5%) when AQ molecules are presumably aggregated, these steric factors disappear, and AQ aggregates lead to the helix unwinding by decreasing the orientational order (since $d\lambda_{\max}/dT$ is positive).

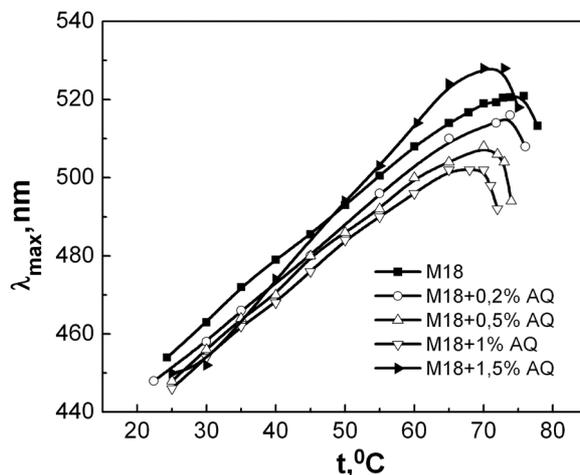


FIGURE 1 Selective reflection maximum as a function of the temperature for cholesteric matrix M18 doped with AQ.

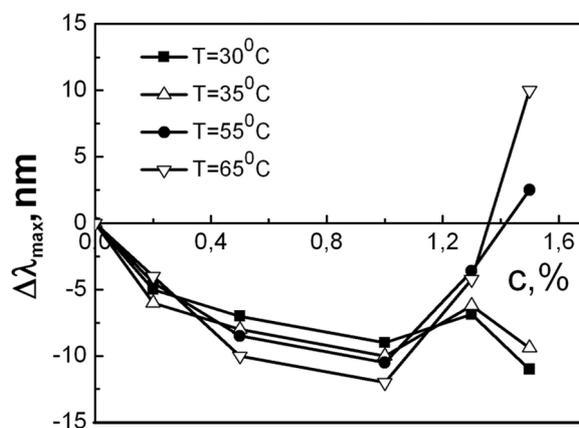


FIGURE 2 Shifts of λ_{\max} with respect to its value in non-doped cholesteric matrix M18 upon the addition of AQ at different temperatures within the cholesteric mesophase range.

The dependences of λ_{\max} on the temperature and the AQ concentration in M19 are shown in Figure 3.

Like the previous case, λ_{\max} decreases upon the introduction of AQ; however, unlike the behavior in M18, this decrease is fully explained by a lowering of the orientational order by a non-mesogenic dopant ($d\lambda_{\max}/dT < 0$).

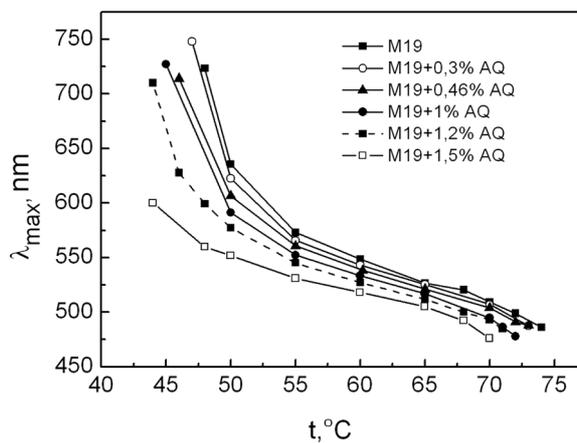


FIGURE 3 Selective reflection maximum as a function of the temperature for cholesteric matrix M18 doped with AQ.

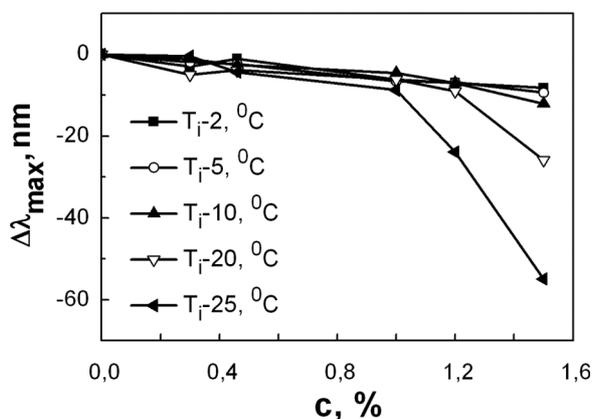


FIGURE 4 Shifts of λ_{\max} with respect to its value in non-doped cholesteric matrix M19 upon the addition of AQ at temperatures by several degrees below the cholesteric-isotropic transition point for the respective composition.

The measured changes in λ_{\max} as compared with those for the initial matrix are shown in Figure 4 as functions of the AQ concentration at different temperatures. Substantial deviations of $\Delta\lambda_{\max}(C)$ from linearity can be noted for higher ($>1\%$) concentrations of AQ at temperatures not too close to T_i . This can be naturally related to the formation of AQ aggregates which can be considered as “new” non-mesogenic components different from individual AQ molecules. These aggregates can become less stable at higher temperatures, where the linearity of $\Delta\lambda_{\max}(C)$ persists in the whole concentration range.

In addition to information on the helical pitch p and its dependence on the NMD concentration, the selective reflection spectra can provide us with one more way of studying the effects of NMD on helically twisted matrices. Along with the well-known relation $\lambda_{\max} = np$, where n is the average refractive index, a similar relation $\Delta\lambda = \Delta np$ also holds ($\Delta\lambda$ is the width of the selective reflection band, and Δn is birefringence). The value of Δn is determined, on the one hand, by the chemical structure of molecules (for non-aromatic nematics or steroid cholesterics, Δn is substantially lower than that for typical nematics with benzene rings, e.g., cyanobiphenyls, and induced cholesterics on their base). On the other hand, Δn essentially depends upon the orientational order parameter, by decreasing accordingly in approaching the isotropic transition. Our approach was similar to [23], where, starting from the selective reflection spectra and the FWHM values, the dependences of Δn on the concentration of NMD introduced into a cholesteric matrix were obtained.

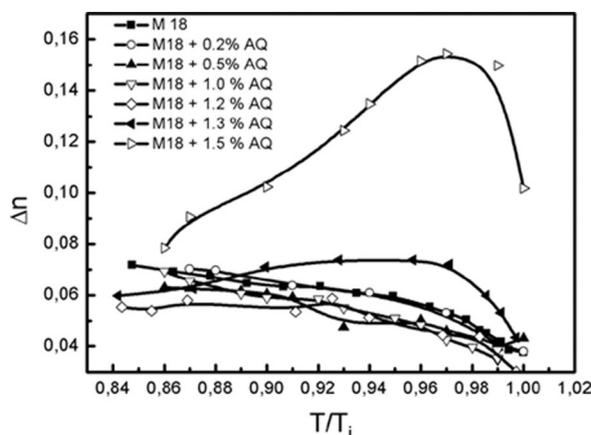


FIGURE 5 Relative birefringence calculated from the selective reflection spectra for cholesteric matrix M18 doped with AQ as a function of the reduced temperature (T_i in K is the temperature of the cholesteric-isotropic phase transition).

The values of Δn shown below were calculated as $\Delta\lambda/\lambda_{\max}$, i.e., FWHM divided by the value of λ at the middle of the selective reflection band. These calculated values of Δn , in fact, correspond to the real birefringence Δn divided by the average refractivity index n ; as in most works on cholesterics, we neglected possible small variations of n .

The calculated values of Δn for matrices M18 and M19 doped by AQ are shown in Figures 5 and 6. The difference in Δn for non-doped matrices is related to their chemical composition (aromatic M19 and non-aromatic M18). The lowering of Δn with the temperature (which becomes stronger close to the isotropic transition temperature) is related to the lowering of the orientational order parameter and a respective decrease in optical anisotropy (birefringence).

At low concentrations, the introduction of AQ causes no substantial changes in Δn , and the character of the temperature dependence of Δn remains the same. At higher AQ concentrations, the picture becomes different – Δn increases noticeably for both matrices, and the temperature dependence becomes qualitatively different. This can be naturally related to the formation of AQ supramolecular aggregates, which also causes changes in the behavior of λ_{\max} noted above (Figs. 2 and 4).

The non-monotonous character of the temperature dependence of Δn for higher AQ concentrations can be explained as follows. At the initial stage of increase in the temperature, the AQ aggregates make the system microheterogeneous (colloidal) with a respective broadening

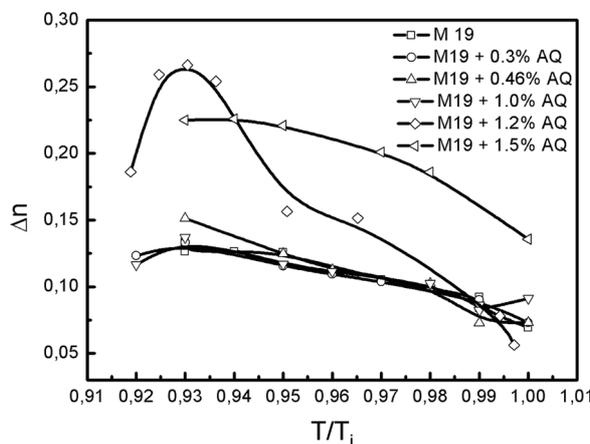


FIGURE 6 Relative birefringence calculated from the selective reflection spectra for cholesteric matrix M19 doped with AQ as a function of the reduced temperature (T_i in K is the temperature of the cholesteric-isotropic phase transition).

of the peaks. Then, when the isotropic transition temperature is approached, the decreasing orientational order becomes predominant (this effect is unusually strong because of the microheterogeneous character of the system).

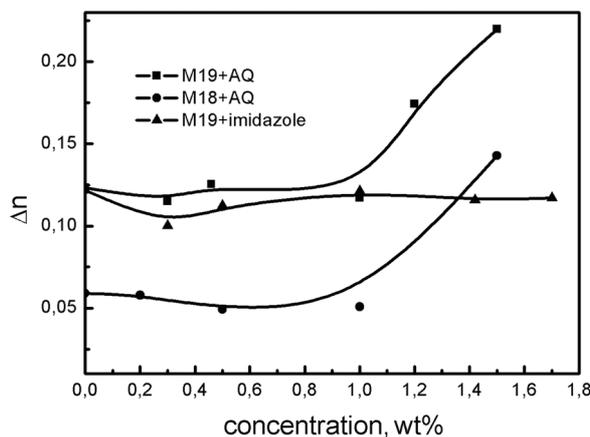


FIGURE 7 Relative birefringence calculated from the selective reflection spectra for cholesteric matrices M18 and M19 doped with AQ and M19 doped with imidazole as a function of the dopant concentration at $T/T_i = 0.95$.

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Figure 7 shows the calculated values of Δn for both matrices as functions of the AQ concentration at $T/T_i = 0.95$. The increase in Δn at AQ concentrations above 1% can be naturally attributed to the formation of supramolecular aggregates of AQ. For comparison, a similar dependence obtained under the same conditions with imidazole as a non-mesogenic dopant is shown. Such a behavior (and even slight decreases in Δn) is typical of non-mesogenic dopants forming real solutions in cholesteric solvents.

CONCLUSIONS

We have shown that the temperature-dependent selective reflection spectra in the cholesteric phase can give a substantial information on the behavior features of non-mesogenic dopants in liquid crystal matrices. Thus, the formation of supramolecular aggregates of anthraquinone dyes is clearly reflected in the concentration dependences of the helical pitch and the relative birefringence. The use of different cholesteric matrices can give a further insight into the mechanisms of intermolecular interactions in complex mesomorphic systems.

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