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Absorption and Fluorescence Measurements in Compensated Cholesteric Mesophases

Part I: Orientation of Chromophores in Liquid Crystal Solvents

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A mixture of cholesteric compounds of opposite helical twisting power at a definite temperature T_n gets nematic properties because the long molecular axes take a parallel arrangement. If the sample is placed between lecithin-treated quartz plates the long axes at T_n switch by an angle of 90° into a direction normal to the cover surfaces. As the orientation of the cholesteric molecules is transferred to the anisotropic solute molecules this effect has been detected by means of measurement of absorptivity and fluorescence efficiency of soluted chromophores. By the method described a possibility opens to determine the direction of optical transitions by a very simple technique.

1. Introduction

It is well known that in nematic liquid crystals the long axes of the molecules adhere in a parallel orientation to the supporting surface (homogeneous texture) when the cover plates had been rubbed before[1]. The same holds for molecules within a cholesteric mesophase of so-called "disturbed texture"[2]. In nematics however, the long axes adopt an orientation perpendicular to the surface of the substrate (homeotropic texture) when the plates are treated with lecithin[3]. A liquid crystal of nematic properties can be obtained at a specific temperature T_n by mixing two cholesterics of opposite helical twisting power in a definite ratio of mixture (compensated cholesteric mixture)[4]. The question arises if the orientation of the molecular axes referred above is obtained in a compensated mixture at T_n on treating the substrate with lecithin. That implies an overturn of the long axes from a parallel to a normal position with respect to the surface.

As in cholesteric and nematic solvents rodlike non-mesomorphic molecules on an average tend to align with their long axes in a parallel fashion with respect to those of the solvent molecules[5, 6], a change of orientation is expected also to apply to solute molecules. If chromophoric molecules are used as a solute the temperature dependence of orientation might be observed by means of absorption and fluorescence measurements, respectively. The results are checked by polarisation microscopy.

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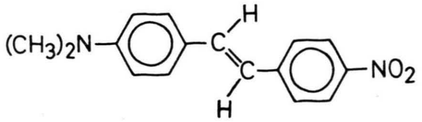
2. Experimental

Measurements of absorption and fluorescence properties of trans-p-dimethyl-amino-p′-nitrostilbene (DANS) were performed in mixtures of cholesteryl chloride (CC) and cholesteryl nonanoate (CN). Concentrations of



DANS

DANS: 10^{-3} weight percent. The absorption spectra were recorded on a Beckman DK 2 spectrophotometer. Surface fluorescence was detected by a Turner Model 210 fluorometer, excitation wavelength 430 nm. The samples were sandwiched between polished quartz plates using 20 μm lead spacers and temperature controlled sample holders (0.1°). The quartz plates were treated with an etheric solution of lecithin before introducing the sample.

The temperatures T_n at which the cholesteric mixtures used compensate were determined by polarisation microscopy (Leitz Labolux-Pol with heating stage):

Table 1.

Mixture	Ratio CC/CN (by weight)	T_n (°C)	T_c (°C)
I	1 : 0.7	55.5	68.5
II	1 : 0.8	60.5	68.0

3. Results and Discussion

The maximum of the longest wavelength absorption band of DANS in CC/CN is centered at 432 nm, that of the fluorescence band in the region of 525 to 545 nm. In part A of Fig. 1 and 2 (solid line) the absorptivity of DANS in CC/CN at 432 nm versus temperature is given. The sharp minimum of absorptivity at 55.5 and 60.5 °C for mixtures I and II, respectively, is obvious. These temperatures correspond to the values of T_n at which the helix senses of CC and CN compensate (see Table 1). Above and below T_n the absorption is rather constant, decreasing at the clearing point T_c and remaining constant in the isotropic state.

Similar results had been obtained in fluorescence measurements. Part B of Fig. 1 and 2 shows the fluorescence yield of DANS in CC/CN versus temperature. The yield slowly decreases with rising temperature, but in the vicinity of T_n a deep minimum occurs.

The minimum of absorptivity and fluorescence yield at T_n can be explained as follows: At $T < T_n$

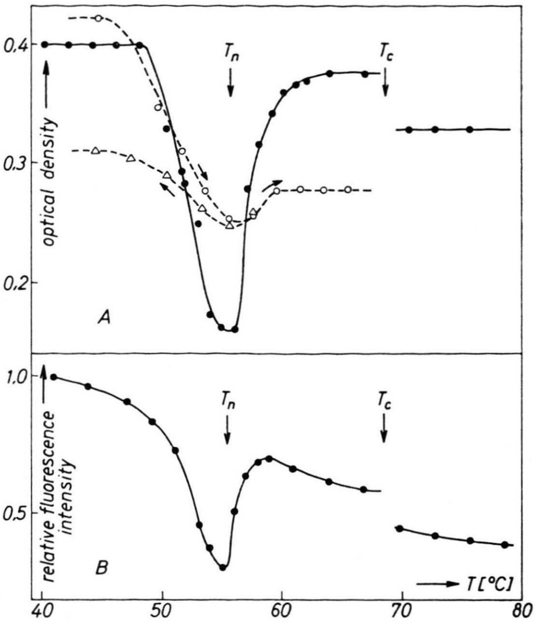


Fig. 1. A) Temperature dependence of optical density at 432 nm of DANS (10^{-3} weight percent) in cholesteryl chloride/cholesteryl nonanoate (1 : 0.7 per weight). Solid line: between lecithin-treated quartz plates, dashed line: without lecithin. B) Temperature dependence of relative fluorescence intensity (related to 40 °C) at 525—545 nm, excitation wavelength 430 nm.

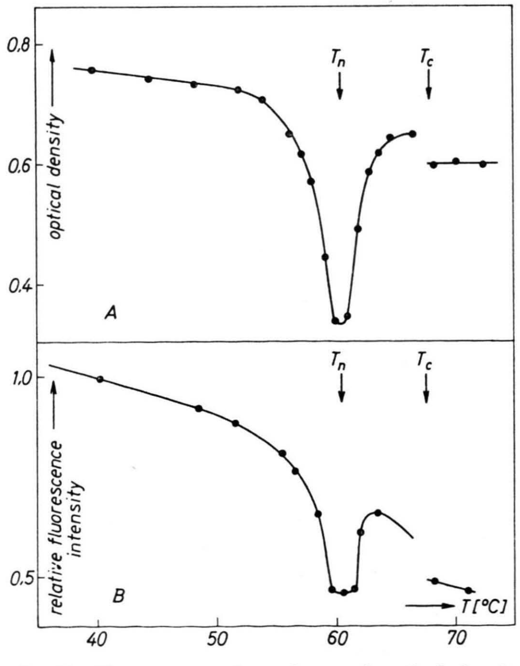


Fig. 2. A) Temperature dependence of optical density at 432 nm of DANS (10^{-3} weight percent) in cholesteryl chloride/cholesteryl nonanoate (1 : 0.8 per weight). B) Temperature dependence of relative fluorescence intensity (related to 40 °C) at 525—545 nm, excitation wavelength 430 nm.

the long axes of the cholesteric molecules are arranged in planes parallel to the surface of the quartz plates. Because of the perpendicular incidence of light the long axes of the solvent molecules as well as those of the solute ones are orientated normal to the propagation direction of the light waves. Furthermore, the low energy electronic transition moment of DANS is polarized parallel to the long axis[7], and thus maximum absorptivity at 432 nm and – because of maximum excitation – maximum fluorescence efficiency is obvious. On approaching T_n the long axes of the solvent molecules, by the influence of lecithin, switch into an arrangement normal to the surface and thus parallel to the direction of incident light.

The same applies to the long axes of DANS molecules. This orientation implies minimum interaction with the electric vector of light and therefore explains the minimum of absorptivity and fluorescence yield at T_n. At $T > T_n$ the molecules return to an orientation as before, and thus the same optical behaviour as at $T < T_n$ holds.

In the isotropic state the long axes are orientated completely at random. Therefore, the absorptivity is less than in the cholesteric state at $T \gtrless T_n$. These results have been confirmed by polarization microscopy. At $T \gtrless T_n$ the highly ordered Grandjean plane texture ("disturbed texture") occurs recognized by its extremely strong optical rotatory power. This observation is in agreement with the almost equal absorptivity in the vicinity of T_n (see part A in Fig. 1 and 2, solid line). Approaching T_n the Grandjean pattern disappears more and more until at T_n total darkness is observed between crossed polarizers.

As the nematic homeotropic texture has now been formed with the long axes perpendicular to the surface the direction of observation is parallel to the optical axis of the uniaxial sample without any optical rotation and birefringence.

The influence of lecithin on the orientation of rodlike molecules is not completely apparent until now. The reason of the "orientation power" may be seen in the amphiphilic character of the molecule. The formation of a lyotropic mesophase in the presence of water is well known[8]. On the quartz surface a monomolecular layer of lecithin may built up with the paraffin chains of the fatty acid groups pointing off the surface. By means of intermolecular forces an assembly of parallely fashioned molecules of a nematic phase prefers to attach to such a brush-like surface rather end to end than perpendicular to the paraffin chains of the lecithin molecules.

Using untreated quartz surfaces the Grandjean texture instantly forms but approaching T_n changes to the Schlieren texture[9]. The cholesteric focal-conic texture arises above T_n being preserved after passing the nematic point repeatedly by decreasing or increasing temperature, respectively. Therefore, corresponding absorption measurements on DANS (without lecithin) would be expected to yield unchanged optical density below T_n. On the other hand, the formation of the undisturbed texture should be indicated by decreasing absorptivity attributed to the inclined arrangement of molecules in focal-conic domains. These suggestions have been confirmed by our results (see Fig. 1 A, dashed line). Because of the Grandjean texture the absorptivity is high at the beginning of the experiment. On increasing temperature it decreases resulting in a shallow minimum at T_n which indicates a slight tendency towards normal orientation. On decreasing temperature the optical density in the region $T < T_n$ remains less than at the beginning of the experiment even on repeated heating and cooling cycles. The difference to the homeotropic alignment achieved with lecithin is quite obvious.

4. Conclusions

Our results show the following: Due to the influence of lecithin-treated surfaces in compensated cholesteric mixtures two different molecular orientations with the long axes being perpendicular to each other can be obtained only by temperature variation. This orientation of the solvent molecules is transferred to that of the anisotropic solute ones and enables to distinguish between parallel and perpendicular direction of electronic transition moments with respect to the long axis of the molecule. One has to compare only fluorescence intensity or optical density of dissolved molecules once with long axes normal and once parallel to the incident light. It should be mentioned that mixtures of cholesteryl esters are transparent down to about 250 nm. Thus, the technique described allows to get informations on the absolute orientation of transition moments in molecules while measurements of fluorescence polarization in isotropic solvents only yield the relative ones[10]. It has the following advantages compared with other methods previously described (e. g. see Ref. [11]) : no use of electric or magnetic fields, no loss of light intensity by polarizers.

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