

Circular dichroism in absorbing mixtures with a cholesteric structure

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This paper is devoted to a study of circular dichroism in nematic-chiral mixtures with a dye. It is shown that the absorption is suppressed in the region where the wavelengths of the selective light scattering coincide with the absorption region of the liquid crystal for circular polarization whose sign is the same as that of the crystal rotation.

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We investigated the circular dichroism induced in nematic-chiral mixtures with a dye. A mixture of esters and ROTN 103, supplied by the H. Hoffmann-La Roche firm, which is transparent in the visible spectrum, was used as the nematic. The aromatic ester of *L*-menthol with a large spiral induction strength, supplied by Z. M. Elashvili, was used as the optically active additive (OAD). The dye was *p*-nitro-benzene-bis(benzolazo)-*p*'-dimethylaniline, provided by E. I. Kovshev. All measurements were performed at a cell thickness of 11.3 μm , a temperature of 19.5 $^{\circ}\text{C}$ and at a 1% dye concentration. The molecules were oriented by rubbing the substrates in one direction.

The circular dichroism was calculated by using the formula $D = (I_l - I_r)/(I_l + I_r)$, where I_l and I_r are the measured transmission coefficients of left-hand and right-hand circularly polarized light, respectively. By varying the OAD concentration, we obtained a spiral pitch far from the region of dye absorption ($p = 1.08 \mu\text{m}$) and in the absorption region. The obtained results are denoted by crosses in Fig. 1. The minima on the curves in Figs. 1b, 1c, and 1d correspond to regions of selective reflection of left-hand circularly polarized light. As seen in Fig. 1, the sign of D changes on the short-wave side. Such dependence of the circular dichroism on the wavelength is attributable to the fact that because of the spiral structure in the molecular arrangement, the absorption of light with a diffracting polarization (in this case a left-hand polarization) changes dramatically near the region of selective reflection. As a result, the diffracting polarization is absorbed more strongly than the nondiffracting polarization on one side of the selective reflection region and it is absorbed more weakly on the other side. As mentioned earlier,¹⁻⁴ this effect is analogous in many respects to the anomalous absorption of x-rays (Bormann effect) that occurs as a result of diffraction in ordinary crystals.

The previously developed theory of the optical properties of absorbing cholesteric liquid crystals^{1,2,4} was used for a quantitative description of the experimental data. The elements of the dielectric constant tensor needed for the calculations in the optical frequency range were determined in the following manner. The real parts were determined from the refractive indices for ordinary and extraordinary rays that were measured directly in a nematic-chiral mixture (without a dye). The imaginary parts respon-

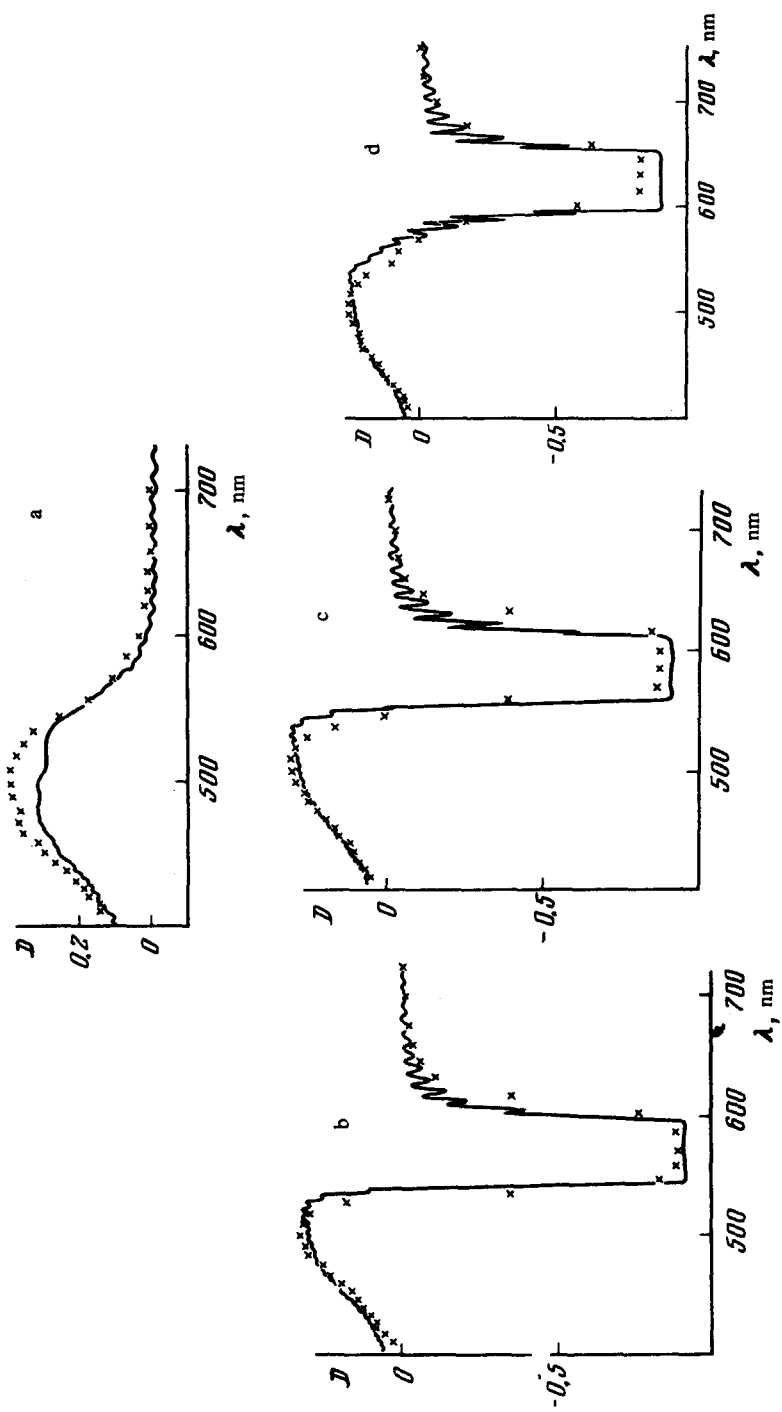


FIG. 1. Circular dichroism in the following mixtures: (a) ROTN 103-91.5%, OAD-7.5%, dye-1%; (b) ROTN 103-85%, OAD-14%, dye-1%; (c) ROTN 103-86%, OAD-13%, dye-1%; (d) ROTN 103-87%, OAD-12%, dye-1%. The solid curve represents theoretical values.

sible for the absorption were determined from the data for light absorption in the nematic phase with the addition of a dye. We assumed that the imaginary parts of the dielectric constant tensor in the chiral phase are the same as those in the original nematic phase (for the same dye concentration). The theoretical values of I_1 and I_r were calculated from the chiral dye parameters measured in this manner by using Eq. (3.8) from Ref. 4, and the theoretical curves for the circular dichroism (Fig. 1) were determined from them. The spiral pitch was chosen in such a way that the theoretically calculated values would be the same as those observed experimentally in the region of selective reflection.

A comparison of the theoretical and experimental curves shows that the theory gives both a qualitative and a quantitative description of the experiment.

It should be mentioned that we took into account in the theoretical calculations the light reflection at the air-glass boundaries. Although this reflection is small ($\sim 5\%$ at each boundary), it produces a qualitative effect: in the absence of such reflection $I_1 \approx 0$ and $D \approx -1$ in the region of selective reflection, whereas the experiment indicates the D differs appreciably from -1 .

In conclusion, we note that the quantitative agreement between the theory and the experiment obtained by us makes it possible to determine all the parameters of the chiral crystal (including those associated with absorption) directly in the chiral phase by selecting from the best fit of the experimental and theoretical curves for the circular dichroism.

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