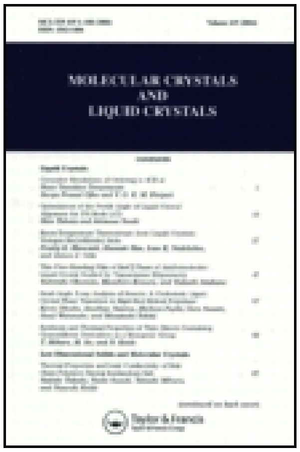

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Determination of the Pitch of a Cholesteric Liquid Crystal by Infrared Transmission Measurements‡

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The pitch of a cholesteric liquid crystal can be inferred from (1) the distance of the Grandjean lines in a wedge type sample[1]; (2) the angular dependence of Bragg-scattering,[2] and (3) the wavelength of maximum reflection.[3] The present paper reports a simple method for determining the pitch based on transmission measurements. It can be particularly valuable in the infrared, i.e. a pitch range of about 0.5 to 5μ, where reflectance measurements are difficult.

A cholesteric liquid crystal characterized by a helix pitch Z can reflect light of a wavelength $\lambda_r \leqslant n(\lambda_r)Z$ where n denotes the refractive index.[3-5] In particular $\lambda_r = n(\lambda_r)Z$ if a parallel light beam propagating parallel to the helix axis is used for the measurement. The latter condition is easily fulfilled with a cholesteric phase displaying the plane texture, where alignment of the helix axis perpendicular to the supporting surfaces is maintained throughout the bulk of the sample by wall forces. The reflectivity arises from the fact that a light beam encounters a change in the refractive index when passing subsequent cholesteric layers which are twisted by a certain angle, except when its electric vector rotates in a sense identical with the screw-sense of the

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helix. Therefore, a circularly polarized wave of opposite rotational sense to the helix experiences the strongest reflection. Interference causes the effect to be most pronounced at $\lambda_r = nZ$. This allows determination of the pitch from the color of the reflected light. The present paper, however, shows that the change in transmittance near λ_r as a result of reflection can also be used as a simple and reliable probe for obtaining absolute values of Z. This change in transmittance due to the helical structure will be referred to as helical absorption, although it must be understood that this is not a true absorption of energy.

All experiments were done with a 1.75 : 1.00 mixture of cholesteryl chloride and cholesteryl myristate (CM). Previous measurements of the optical rotatory power[6] have shown that its pitch is highly temperature sensitive following the relationship $Z(T) = (4.0 \pm 0.2) \times 10^{-3}/(T - T_{\text{nem}})$ (1) for $T < 50°$ with $T_{\text{nem}} = 40.0°$. A 1 mil sample‡ displaying the plane texture was prepared between NaCl windows and inserted into a temperature controlled optical cell. The infrared transmittance was recorded with a Perkin–Elmer 621 IR Spectrophotometer using unpolarized light. It shows a temperature sensitive absorption peak with a half width $\delta\lambda = (0.1 \pm 0.01)\lambda_r$ superimposed on a background absorption arising from vibrational excitation and light scattering§ (Figs. 1 and 2). Analyzing 15 absorption curves and calculating $Z(T)$ from the wavelength λ_r of the absorption peaks, using $Z = \lambda_r/n$ and $n(\lambda_r) = 1.4$, yields pitch values deviating by not more than $\pm 5\%$ from the values derived from measurements of the optical rotatory power (Eq. (1)). This proves that optical " absorption " of the helical structure is observed. For application purposes the method is limited to $Z \lesssim 6\mu$ because the IR spectrum is dominated by molecular

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‡ 1 mil appears to be an optimum layer thickness for a cholesteric structure with $2 < Z < 7\mu$: with $d \geqslant 2$ mil, the plane texture is no longer perfect, giving rise to a broadening of the absorption peak; with $d \leqslant 10\mu$ the absorption becomes too weak.

§ The absorption curve of the isotropic melt can be used as a reference line if one corrects for the reduced Rayleigh-scattering.

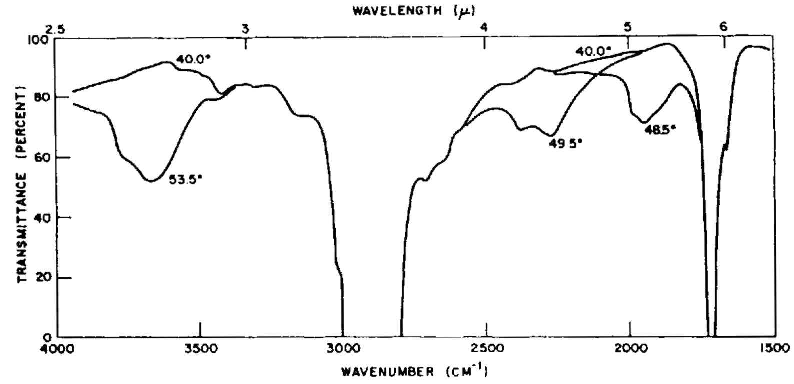

Figure 1. IR transmittance of CM at various temperatures (scale expansion ×2).

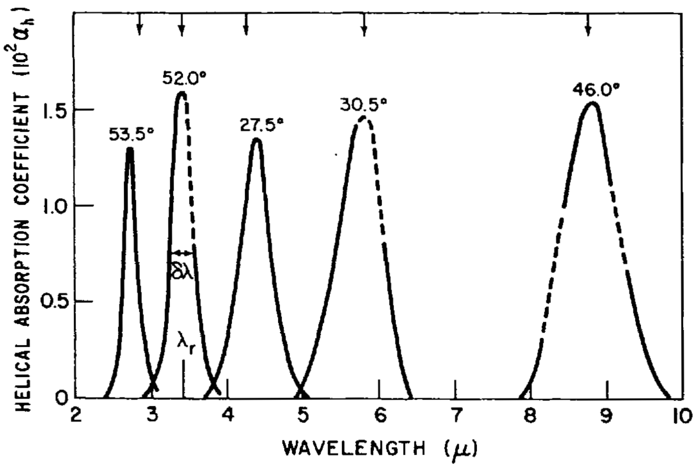

Figure 2. Helical absorption bands of CM at various temperatures. The dashed regions correspond to wavelengths where helical " absorption " is masked by strong vibrational absorption. The arrows indicate the position of the maxima calculated from measurements of the optical rotatory power.

vibration for $\lambda \gtrsim 8\ \mu$. Quantitative analysis of the spectra (Fig. 2) shows that a dimensionless " absorption " coefficient α_h per cycle of the helical structure can be defined: $\alpha_h = (3 \pm 1) \times 10^{-2}$. A layer of thickness d containing $N = d/Z$ cycles has the optical density $D = \alpha_h N$.‡

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‡ Unpolarized light can be regarded as a superposition of two linear polarized waves of equal intensity both of which can be divided into a right- and left-handed circular component. For light polarized circularly and opposite to the helical sense α_h has therefore to be multiplied by a factor of 2.

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